

## **DRY AEROSOL CARPET CLEANING PROCESS**

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### **CROSS REFERENCE TO RELATED APPLICATION**

[0001] The present application is a continuation-in-part application Serial No. 10/458,031 and was filed on June 9, 2003, entitled "Cleaning Tool with Gripping Assembly for a Disposable Scrubbing Head", and incorporated herein, which is a continuation-in-part of U.S. Serial No.10/345,655 filed on January 16, 2003, which is incorporated herein.

### **BACKGROUND OF THE INVENTION**

#### **Field of the Invention**

[0002] The present invention relates generally to aerosol cleaning formulations and aerosol cleaning devices for cleaning carpets and hard surfaces. The present invention relates to cleaning compositions, pads, and implements useful in removing soil from soft and hard surfaces. The present invention relates to methods of cleaning carpets and hard surfaces with aerosol cleaning devices.

#### **Description of the Related Art**

[0003] Aerosol dispensers for delivering cleaners for carpets and other surfaces are well known. Examples of various dispenser designs are disclosed, for example, in U.S. Patent Nos. 2,761,594 to Stroh, 3,138,295 to O'Donnell, 3,269,614 to Henry, 3,373, 908 to Crowell, 3,429,483 to Micallef, 3,642,179 to Micallef, 3,887,115 to Petterson, 4,068,782 to Van der Heijden, 4,378,081 to van Lit, 4,805,839 to Malek, 3,967,763 to Focht, 5,027,986 to Heinzl et al., 6,145,704 to Geier, and 6,398,082 to Clark et al.

[0004] It is therefore an object of the present invention to provide an aerosol cleaner that overcomes the disadvantages and shortcomings associated with prior art cleaners.

### **SUMMARY OF THE INVENTION**

[0005] In accordance with the above objects and those that will be mentioned and will become apparent below, one aspect of the present invention comprises a method of cleaning carpets comprising the steps of:

- a. applying an aerosol carpet cleaning composition to the carpet,
- b. wiping the carpet with a cleaning implement comprising a disposable cleaning substrate, and
- c. allowing the carpet to dry.

[0006] In accordance with the above objects and those that will be mentioned and will become apparent below, another aspect of the present invention comprises an aerosol carpet cleaning composition, wherein said composition penetrates a nylon carpet with fiber length 0.50 inches less than 0.50 inches under spray only conditions.

[0007] In accordance with the above objects and those that will be mentioned and will become apparent below, another aspect of the present invention comprises An article of manufacture comprising:

- a. a cleaning implement;
- b. a disposable cleaning pad;
- c. an aerosol cleaning composition; and
- d. a set of instructions comprising the steps of:
  - i. applying an aerosol carpet cleaning composition to the carpet,
  - ii. wiping the carpet with a cleaning implement comprising a disposable cleaning substrate, and
  - iii. allowing the carpet to dry.

#### DETAILED DESCRIPTION OF THE INVENTION

[0008] Before describing the present invention in detail, it is to be understood that this invention is not limited to particularly exemplified systems or process parameters that may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments of the invention only, and is not intended to limit the scope of the invention in any manner.

[0009] All publications, patents and patent applications cited herein, whether *supra* or *infra*, are hereby incorporated by reference in their entirety to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated by reference.

[0010] It must be noted that, as used in this specification and the appended claims, the singular forms “a,” “an” and “the” include plural referents unless the content clearly dictates otherwise. Thus, for example, reference to a “surfactant” includes two or more such surfactants.

[0011] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention pertains. Although a number of methods and materials similar or equivalent to those described herein can be used in the practice of the present invention, the preferred materials and methods are described herein.

[0012] The cleaning compositions can be used as a disinfectant, sanitizer, and/or sterilizer. As used herein, the term "disinfect" shall mean the elimination of many or all pathogenic microorganisms on surfaces with the exception of bacterial endospores. As used herein, the term "sanitize" shall mean the reduction of contaminants in the inanimate environment to levels considered safe according to public health ordinance, or that reduces the bacterial population by significant numbers where public health requirements have not been established. An at least 99% reduction in bacterial population within a 24 hour time period is deemed "significant." As used herein, the term "sterilize" shall mean the complete elimination or destruction of all forms of microbial life and which is authorized under the applicable regulatory laws to make legal claims as a "Sterilant" or to have sterilizing properties or qualities.

[0013] In the application, effective amounts are generally those amounts listed as the ranges or levels of ingredients in the descriptions, which follow hereto. Unless otherwise stated, amounts listed in percentage ("%s") are in weight percent (based on 100% active) of the cleaning composition alone, not accounting for the substrate weight. Each of the noted cleaner composition components and substrates is discussed in detail below.

[0014] As used herein, the term "cleaning substrate" is intended to include any woven, nonwoven or foam substrate which is used to clean an article or a surface. Examples of cleaning substrates include, but are not limited to, mitts, webs of material containing a single sheet, composites, or multiple layer laminates of material which is used to clean a surface by hand or a sheet of material which can be attached to a cleaning implement, such as a floor mop, handle, or a hand held cleaning tool, such as a toilet cleaning device.

[0015] As used herein, "wiping" refers to any shearing action that the substrate undergoes while in contact with a target surface. This includes hand or body motion, substrate-implement motion over a surface, or any perturbation of the substrate via energy sources such as ultrasound, mechanical vibration, electromagnetism, and so forth.

[0016] The term "sponge", as used herein, is meant to mean an elastic, porous material, including, but not limited to, compressed sponges, cellulosic sponges, reconstituted cellulosic sponges, cellulosic materials, foams from high internal phase emulsions, such as those disclosed in U. S. Pat. 6,525,106, polyethylene, polypropylene, polyvinyl alcohol, polyurethane, polyether, and polyester sponges, foams and nonwoven materials, and mixtures thereof.

[0017] The term "cleaning composition", as used herein, is meant to mean and include a cleaning formulation having at least one surfactant.

[0018] The term "surfactant", as used herein, is meant to mean and include a substance or compound that reduces surface tension when dissolved in water or water solutions, or that reduces interfacial tension between two liquids, or between a liquid and a solid. The term "surfactant" thus includes anionic, nonionic and/or amphoteric agents.

#### Cleaning Implement

[0019] In an embodiment of the invention, the aerosol cleaning container is used with a cleaning implement. In an embodiment of the invention, the aerosol cleaning container is attached to a cleaning implement. In an embodiment of the invention, the aerosol cleaning container is removably attached to a cleaning implement. In an embodiment of the invention, cleaning implement comprises the tool assembly disclosed in Co-pending Application U.S. Serial No.10/345,655 filed on January 16, 2003, entitled "Cleaning Tool with Gripping Assembly for a Disposable Scrubbing Head", and incorporated herein.

[0020] In another embodiment of the invention, the cleaning implement comprises the tool assembly disclosed in Co-pending Application Serial No. 10/458,031 and was filed on June 9, 2003, entitled "Cleaning Tool with Gripping Assembly for a Disposable Scrubbing Head", and incorporated herein.

[0021] In an embodiment of the invention, the aerosol cleaning container is used with a cleaning substrate. The cleaning substrate may be disposable. The cleaning substrate may be attached to a cleaning implement. A wide variety of materials can be used as the substrate. Examples include, nonwoven substrates, wovens substrates, hydroentangled substrates, foams and sponges.

#### Substrate

[0022] The substrate can include both natural and synthetic fibers. The substrate can be composed of suitable unmodified and/or modified naturally occurring fibers including cotton, Esparto grass, bagasse, hemp, flax, silk, wool, wood pulp, chemically modified wood pulp, jute, ethyl cellulose, and/or cellulose acetate. Various pulp fibers can be utilized including, but not limited to, thermomechanical pulp fibers, chemi-thermomechanical pulp fibers, chemi-mechanical pulp fibers, refiner mechanical pulp fibers, stone groundwood pulp fibers, peroxide mechanical pulp fibers and so forth.

[0023] Suitable synthetic fibers can comprise fibers of one, or more, of polyvinyl chloride, polyvinyl fluoride, polytetrafluoroethylene, polyvinylidene chloride, polyacrylics such as ORLON®, polyvinyl acetate, Rayon®, polyethylvinyl acetate, non-soluble or soluble polyvinyl alcohol, polyolefins such as polyethylene (e.g., PULPEX®) and polypropylene, polyamides such as nylon, polyesters such as DACRON® or KODEL®, polyurethanes, polystyrenes, and the like, including fibers comprising polymers containing more than one monomer.

[0024] Various forming methods can be used to form a suitable fibrous web. For instance, the web can be made by nonwoven dry forming techniques, such as air-laying, or alternatively by wet laying, such as on a paper making machine. Other non-woven manufacturing techniques, including but not limited to techniques such as melt blown, spunbonded, needle punched, and hydroentanglement methods can also be used. In one embodiment, the dry fibrous web can be an airlaid nonwoven web comprising a combination of natural fibers, staple length synthetic fibers and a latex binder. The dry fibrous web can be about 20- 80 percent by weight wood pulp fibers, 10-60 percent by weight staple length polyester fibers, and about 10-25 percent by weight binder.

[0025] The cleaning substrate of this invention may be a multilayer laminate and may be formed by a number of different techniques including but not limited to using adhesive, needle punching, ultrasonic bonding, thermal calendering and through-air bonding. Such a multilayer laminate may be an embodiment wherein some of the layers are spunbond and some meltblown such as a spunbond/meltblown/spunbond (SMS) laminate as disclosed in U.S. Pat. No. 4,041,203 to Brock et al. and U.S. Pat. No. 5,169,706 to Collier, et al., each hereby incorporated by reference. The SMS laminate may be made by sequentially depositing onto a moving conveyor belt or forming wire first a spunbond web layer, then a meltblown web layer and last another spunbond layer and then bonding the laminate. Alternatively, the three web layers may be made individually, collected in rolls and combined in a separate bonding step.

[0026] The following patents<sup>1</sup> are incorporated herein by reference for their disclosure related to webs: U.S. Pat. No. 3,862,472; U.S. Pat. No. 3,982,302; U.S. Pat. No. 4,004,323; U.S. Pat. No. 4,057,669; U.S. Pat. No. 4,097,965; U.S. Pat. No. 4,176,427; U.S. Pat. No. 4,130,915; U.S. Pat. No. 4,135,024; U.S. Pat. No. 4,189,896; U.S. Pat. No. 4,207,367; U.S. Pat. No. 4,296,161; U.S. Pat. No. 4,309,469; U.S. Pat. No. 4,682,942; U.S. Pat. No. 4,637,859; U.S. Pat. No. 5,223,096; U.S. Pat. No. 5,240,562; U.S. Pat. No. 5,556,509; and U.S. Pat. No. 5,580,423.

[0027] The substrate may also contain superabsorbent materials. A wide variety of high absorbency materials (also known as superabsorbent materials) are known to those skilled in the art. See, for example, U.S. Pat. No. 4,076,663 issued Feb. 28, 1978 to Masuda et al, U.S. Pat. No. 4,286,082 issued Aug. 25, 1981 to Tsubakimoto et al., U.S. Pat. No. 4,062,817 issued Dec. 13, 1977 to Westerman, and U.S. Pat. No. 4,340,706 issued Jul. 20, 1982 to Obayashi et al. The absorbent capacity of such high-absorbency materials is generally many times greater than the absorbent capacity of fibrous materials. For example, a fibrous matrix of wood pulp fluff can absorb about 7-9 grams of a liquid, (such as 0.9 weight percent saline) per gram of wood pulp fluff, while the high-absorbency materials can absorb at least about 15, preferably at least about 20, and often at least about 25 grams of liquid, such as 0.9 weight percent saline, per gram of the high-absorbency material. U.S. Pat. No. 5,601,542, issued to Melius et al., discloses an absorbent article in which superabsorbent material is contained in layers of discrete pouches. Alternately, the superabsorbent material may be within one layer or dispersed throughout the substrate.

[0028] The substrate can include an absorbent core reservoir with a large capacity to absorb and retain fluid. The total absorbency of the substrate can be measured according to the method below.

**[0029] Total Absorbency “Dunk and Drain” Method**

Weigh 4” X 4” samples dry = Dry wt. Place samples in container (large enough to completely immerse samples) with DI water for 5 minutes. Remove from DI water with tongs or tweezers and clip on corner with the suspended binder clip. Allow sample to drain while suspended for 5 minutes. Record sample weight after 5 minutes = Wet wt.

Calculations: Total Absorbency in g/g = (Wet wt – Dry wt.)/ Wet wt.

Substrates of the present invention may have total absorbency greater than 5 g/g.

Substrates of the present invention may have total absorbency greater than 10 g/g.

Substrates of the present invention may have total absorbency greater than 15 g/g.

**Aerosol Cleaning Canister**

[0030] The cleaning composition is preferably stored in and dispensed from a pressurized, corrosion resistant canister or cleaning fluid container that is equipped with a nozzle so that an aerosol or spray of the composition can be readily applied to a surface as a relatively uniform layer of foam. As used herein, the terms “aerosol” and “spray” denote a suspension of fine solid or liquid particles. Suitable aerosol canisters or dispensers include a sealed chamber where cleaning fluid and propellant are stored and a hollow stem or tube having a distal end located within the chamber and a proximal end outside. The proximal end is connected to nozzle with an orifice appropriately dimensioned to create a fan-shaped spray pattern. Flow of cleaning fluid and propellant through the stem is regulated by a valve that is typically pressure activated. A suitable nozzle comprises a vertical valve having a rectangular orifice with dimensions of 0.010 in. (0.254 mm) x 0.031 in. (0.787 mm) that is manufactured by Summit Packaging System, Inc., Manchester, NH. Aerosol dispensers are well known in the art. Although pressure within the dispenser does not appear to be critical, a preferred range is about 40 to 58 lb./in.<sup>2</sup> more preferably 40 to 50 lb./in.<sup>2</sup> and most preferably 40 to 47 lb./in.<sup>2</sup> at 70°F (21°C).

[0031] The aerosol dispensers are constructed of conventional materials. The dispenser should be capable of withstanding internal pressure in the range of from about 20 to about 110 psig and more preferably from about 20 to about 70 psig. The dispenser dispenses the carpet cleaning composition as a spray of very fine, or finely divided, particles or droplets. The composition may be dispensed as a foam. See, D.J. Durian, "Foams," *Kirk-Othmer Encyclopedia of Chemical Technology* (1994).

[0032] The aerosol dispenser is pressurized with a gaseous component that is generally known as a propellant. Common aerosol propellants, e.g., gaseous hydrocarbons such as isobutane, and mixed halogenated hydrocarbons, can be used. Halogenated hydrocarbon propellants such as chlorofluoro hydrocarbons have been alleged to contribute to environmental problems, and are not preferred. When cyclodextrin is present in the carpet cleaning composition for odor control reasons, hydrocarbon propellants are not preferred, because they can form complexes with the cyclodextrin molecules thereby reducing the availability of uncomplexed cyclodextrin molecules for odor absorption. Preferred propellants are compressed air, nitrogen, carbon dioxide, and other inert gases. Commercially available aerosol-spray dispensers are further described in U.S. Patent Nos. 3,436,772 to Stebbins and 3,600,325 to Kaufman et al., both of which are incorporated herein by reference.

[0033] Another type of aerosol dispenser that may be employed includes a barrier that separates the cleaning composition from the propellant, e.g., compressed air or nitrogen, which is further described in U.S. Patent No. 4,260,110 to Werding and incorporated herein by reference. Such a dispenser is available from EP Spray Systems, East Hanover, NJ.

[0034] Alternatively, the aerosol spray dispenser can be a self-pressurized non-propellant container having a convoluted liner and an elastomeric sleeve. These self-pressurized dispensers employ a liner/sleeve assembly containing a thin, flexible radially expandable convoluted plastic liner, which is about 0.010 in. (0.254 mm) to about 0.020 in. (0.508 mm) thick, inside an essentially cylindrical elastomeric sleeve. The liner/sleeve is capable of holding a substantial quantity of cleaning composition product and of causing the product to be dispensed. Suitable self-pressurized spray dispensers are further described



in U.S. Patent Nos. 5,111,971 and 5,232,126 both to Winer and which are herein incorporated by reference.

#### Cleaning composition

[0035] The cleaning composition may contain one or more surfactants selected from anionic, nonionic, cationic, ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof. A typical listing of anionic, nonionic, ampholytic, and zwitterionic classes, and species of these surfactants, is given in U.S. Pat. 3,929,678 to Laughlin and Heuring. A list of suitable cationic surfactants is given in U.S. Pat. 4,259,217 to Murphy. Where present, ampholytic, amphoteric and zwitterionic surfactants are generally used in combination with one or more anionic and/or nonionic surfactants. The surfactants are present at a level of from about 0% to 10%, or from 0.001% to 5%, or from 0.01% to 0.5% by weight.

[0036] The cleaning composition may comprise an anionic surfactant. Essentially any anionic surfactants useful for detergative purposes can be comprised in the cleaning composition. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and tri-ethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic surfactants may comprise a sulfonate or a sulfate surfactant. Anionic surfactants may comprise an alkyl sulfate, a linear or branched alkyl benzene sulfonate, or an alkyldiphenyloxide disulfonate, as described herein.

[0037] Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (for instance, saturated and unsaturated C12- C18 monoesters) diesters of sulfosuccinate (for instance saturated and unsaturated C6-C14 diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil. Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C5-C17acyl-N-

(C1-C4 alkyl) and -N-(C1-C2 hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysacchanides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein). Alkyl sulfate surfactants may be selected from the linear and branched primary C10-C18 alkyl sulfates, the C11-C15 branched chain alkyl sulfates, or the C12-C14 linear chain alkyl sulfates.

[0038] Alkyl ethoxysulfate surfactants may be selected from the group consisting of the C10-C18 alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. The alkyl ethoxysulfate surfactant may be a C11-C18, or a C11-C15 alkyl sulfate which has been ethoxylated with from 0.5 to 7, or from 1 to 5, moles of ethylene oxide per molecule. One aspect of the invention employs mixtures of the alkyl sulfate and/ or sulfonate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

[0039] Anionic sulfonate surfactants suitable for use herein include the salts of C5-C20 linear alkylbenzene sulfonates, alkyl ester sulfonates, C6-C22 primary or secondary alkane sulfonates, C6-C24 olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof. Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein. Suitable alkyl ethoxy carboxylates include those with the formula  $RO(CH_2CH_2O)_xCH_2COO^-M^+$  wherein R is a C6 to C18 alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20 % and M is a cation. Suitable alkyl polyethoxypolycarboxylate surfactants include those having the formula  $RO-(CHR^1-CHR^2-O)-R^3$  wherein R is a C6 to C18 alkyl group, x is from 1 to 25,  $R^1$  and  $R^2$  are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and  $R^3$  is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

[0040] Suitable soap surfactants include the secondary soap surfactants, which contain a carboxyl unit connected to a secondary carbon. Suitable secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-

soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid. Certain soaps may also be included as suds suppressors.

**[0041]** Other suitable anionic surfactants are the alkali metal sarcosinates of formula  $R-CON(R^1)CH_2COOM$ , wherein R is a C5-C17 linear or branched alkyl or alkenyl group,  $R^1$  is a C1-C4 alkyl group and M is an alkali metal ion. Examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

**[0042]** Essentially any alkoxyated nonionic surfactants are suitable herein, for instance, ethoxylated and propoxylated nonionic surfactants. Alkoxyated surfactants can be selected from the classes of the nonionic condensates of alkyl phenols, nonionic ethoxylated alcohols, nonionic ethoxylated/propoxylated fatty alcohols, nonionic ethoxylate/propoxylate condensates with propylene glycol, and the nonionic ethoxylate condensation products with propylene oxide/ ethylene diamine adducts.

**[0043]** The condensation products of aliphatic alcohols with from 1 to 25 moles of alkylene oxide, particularly ethylene oxide and/or propylene oxide, are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Also suitable are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from 2 to 10 moles of ethylene oxide per mole of alcohol.

**[0044]** Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula  $R^2CONR^1Z$  wherein:  $R^1$  is H, C1-C4 hydrocarbyl, 2-hydroxyethyl, 2-hydroxypropyl, ethoxy, propoxy, or a mixture thereof, for instance, C1-C4 alkyl, or C1 or C2 alkyl; and  $R^2$  is a C5-C31 hydrocarbyl, for instance, straight-chain C5-C19 alkyl or alkenyl, or straight-chain C9-C17 alkyl or alkenyl, or straight-chain C11-C17 alkyl or alkenyl, or mixture thereof-, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (for example, ethoxylated or propoxylated) thereof. Z may be derived from a reducing sugar in a reductive amination reaction, for example, Z is a glycityl.

[0045] Suitable fatty acid amide surfactants include those having the formula:

$R^1\text{CON}(R^2)_2$  wherein  $R^1$  is an alkyl group containing from 7 to 21, or from 9 to 17 carbon atoms and each  $R^2$  is selected from the group consisting of hydrogen, C1-C4 alkyl, C1-C4 hydroxyalkyl, and  $-(C_2H_4O)_xH$ , where x is in the range of from 1 to 3.

[0046] Suitable alkylpolysaccharides for use herein are disclosed in U.S. Pat. 4,565,647 to Llenado, having a hydrophobic group containing from 6 to 30 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.3 to 10 saccharide units. Alkylpolyglycosides may have the formula:  $R^2O(C_nH_{2n}O)_t(\text{glycosyl})_x$  wherein  $R^2$  is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18 carbon atoms; n is 2 or 3; t is from 0 to 10, and x is from 1.3 to 8. The glycosyl may be derived from glucose.

[0047] Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids. Suitable amine oxides include those compounds having the formula  $R^3(OR^4)_xNO(R^5)_2$  wherein  $R^3$  is selected from an alkyl, hydroxyalkyl, acylamidopropyl and alkylphenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms;  $R^4$  is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof-, x is from 0 to 5, preferably from 0 to 3; and each  $R^5$  is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Suitable amine oxides are C10-C18 alkyl dimethylamine oxide, and C10-18 acylamido alkyl dimethylamine oxide. A suitable example of an alkyl amphodicarboxylic acid is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

[0048] Zwitterionic surfactants can also be incorporated into the cleaning compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

[0049] Suitable betaines are those compounds having the formula  $R(R^1)_2N^+R^2COO^-$  wherein R is a C6-C18 hydrocarbyl. group, each  $R^1$  is typically C1-C3 alkyl, and  $R^2$  is a C1-C5 hydrocarbyl group. Suitable betaines are C12-18 dimethyl-ammonio hexanoate

and the C10-18 acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

[0050] Suitable cationic surfactants to be used herein include the quaternary ammonium surfactants. The quaternary ammonium surfactant may be a mono C6-C16, or a C6-C10 N-alkyl or alkenyl ammonium surfactant wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups. Suitable are also the mono-alkoxylated and bis-alkoxylated amine surfactants.

[0051] Another suitable group of cationic surfactants, which can be used in the cleaning compositions, are cationic ester surfactants. The cationic ester surfactant is a compound having surfactant properties comprising at least one ester (i.e. -COO-) linkage and at least one cationically charged group. Suitable cationic ester surfactants, including choline ester surfactants, have for example been disclosed in U.S. Pat. No.s 4,228,042, 4,239,660 and 4,260,529. The ester linkage and cationically charged group may be separated from each other in the surfactant molecule by a spacer group consisting of a chain comprising at least three atoms (i.e. of three atoms chain length), or from three to eight atoms, or from three to five atoms, or three atoms. The atoms forming the spacer group chain are selected from the group consisting of carbon, nitrogen and oxygen atoms and any mixtures thereof, with the proviso that any nitrogen or oxygen atom in said chain connects only with carbon atoms in the chain. Thus spacer groups having, for example, -O-O- (i.e. peroxide), -N-N-, and -N-O- linkages are excluded, whilst spacer groups having, for example -CH<sub>2</sub>-O-, CH<sub>2</sub>- and -CH<sub>2</sub>-NH-CH<sub>2</sub>- linkages are included. The spacer group chain may comprise only carbon atoms, or the chain is a hydrocarbyl chain.

[0052] The cleaning composition may comprise cationic mono-alkoxylated amine surfactants, for instance, of the general formula:  $R^1R^2R^3N^+ApR^4X^-$  wherein  $R^1$  is an alkyl or alkenyl moiety containing from about 6 to about 18 carbon atoms, or from 6 to about 16 carbon atoms, or from about 6 to about 14 carbon atoms;  $R^2$  and  $R^3$  are each independently alkyl groups containing from one to about three carbon atoms, for instance, methyl, for instance, both  $R^2$  and  $R^3$  are methyl groups;  $R^4$  is selected from hydrogen, methyl and ethyl;  $X^-$  is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, to provide electrical neutrality; A is a alkoxy group, especially a ethoxy, propoxy or butoxy group; and p is from 0 to about 30, or from 2 to about 15, or from 2 to about 8. The  $ApR^4$

group in the formula may have  $p=1$  and is a hydroxyalkyl group, having no greater than 6 carbon atoms whereby the -OH group is separated from the quaternary ammonium nitrogen atom by no more than 3 carbon atoms. Suitable  $ApR^4$  groups are  $-CH_2CH_2-OH$ ,  $-CH_2CH_2CH_2-OH$ ,  $-CH_2CH(CH_3)-OH$  and  $-CH(CH_3)CH_2-OH$ . Suitable  $R^1$  groups are linear alkyl groups, for instance, linear  $R^1$  groups having from 8 to 14 carbon atoms.

[0053] Suitable cationic mono-alkoxylated amine surfactants for use herein are of the formula  $R^1(CH_3)(CH_3)N^+(CH_2CH_2O)_{2-5}H X^-$  wherein  $R^1$  is C10-C18 hydrocarbyl and mixtures thereof, especially C10-C14 alkyl, or C10 and C12 alkyl, and  $X^-$  is any convenient anion to provide charge balance, for instance, chloride or bromide.

[0054] As noted, compounds of the foregoing type include those wherein the ethoxy  $(CH_2CH_2O)$  units (EO) are replaced by butoxy, isopropoxy  $[CH(CH_3)CH_2O]$  and  $[CH_2CH(CH_3)O]$  units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

[0055] The cationic bis-alkoxylated amine surfactant may have the general formula:  $R^1R^2N^+ApR^3A'qR^4 X^-$  wherein  $R^1$  is an alkyl or alkenyl moiety containing from about 8 to about 18 carbon atoms, or from 10 to about 16 carbon atoms, or from about 10 to about 14 carbon atoms;  $R^2$  is an alkyl group containing from one to three carbon atoms, for instance, methyl;  $R^3$  and  $R^4$  can vary independently and are selected from hydrogen, methyl and ethyl,  $X^-$  is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, sufficient to provide electrical neutrality. A and A' can vary independently and are each selected from C1-C4 alkoxy, for instance, ethoxy, (i.e.,  $-CH_2CH_2O-$ ), propoxy, butoxy and mixtures thereof, p is from 1 to about 30, or from 1 to about 4 and q is from 1 to about 30, or from 1 to about 4, or both p and q are 1.

[0056] Suitable cationic bis-alkoxylated amine surfactants for use herein are of the formula  $R^1CH_3N^+(CH_2CH_2OH)(CH_2CH_2OH) X^-$ , wherein  $R^1$  is C10-C18 hydrocarbyl and mixtures thereof, or C10, C12, C14 alkyl and mixtures thereof,  $X^-$  is any convenient anion to provide charge balance, for example, chloride. With reference to the general cationic bis-alkoxylated amine structure noted above, since in one example compound  $R^1$  is derived from (coconut) C12-C14 alkyl fraction fatty acids,  $R^2$  is methyl and  $ApR^3$  and  $A'qR^4$  are each monoethoxy.

[0057] Other cationic bis-alkoxylated amine surfactants useful herein include compounds of the formula:  $R^1R^2N^+-(CH_2CH_2O)_pH-(CH_2CH_2O)_qX^-$  wherein  $R^1$  is C10-C18 hydrocarbyl, or C10-C14 alkyl, independently  $p$  is 1 to about 3 and  $q$  is 1 to about 3,  $R^2$  is C1-C3 alkyl, for example, methyl, and  $X^-$  is an anion, for example, chloride or bromide.

[0058] Other compounds of the foregoing type include those wherein the ethoxy  $(CH_2CH_2O)$  units (EO) are replaced by butoxy (Bu) isopropoxy  $[CH(CH_3)CH_2O]$  and  $[CH_2CH(CH_3)O]$  units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

[0059] The inventive compositions may include at least one fluorosurfactant selected from nonionic fluorosurfactants, cationic fluorosurfactants, and mixtures thereof which are soluble or dispersible in the aqueous compositions being taught herein, sometimes compositions which do not include further deterative surfactants, or further organic solvents, or both. Suitable nonionic fluorosurfactant compounds are found among the materials presently commercially marketed under the tradename Fluorad® (ex. 3M Corp.) Exemplary fluorosurfactants include those sold as Fluorad® FC-740, generally described to be fluorinated alkyl esters; Fluorad® FC-430, generally described to be fluorinated alkyl esters; Fluorad® FC-431, generally described to be fluorinated alkyl esters; and, Fluorad® FC-170-C, which is generally described as being fluorinated alkyl polyoxyethylene ethanols.

[0060] Suitable nonionic fluorosurfactant compounds include those which is believed to conform to the following formulation:  $C_nF_{2n+1}SO_2N(C_2H_5)(CH_2CH_2O)_xCH_3$  wherein:  $n$  has a value of from 1-12, or from 4-12, or 8;  $x$  has a value of from 4-18, or from 4-10, or 7; which is described to be a nonionic fluorinated alkyl alkoxylate and which is sold as Fluorad® FC-171 (ex. 3M Corp., formerly Minnesota Mining and Manufacturing Co.).

[0061] Additionally suitable nonionic fluorosurfactant compounds are also found among the materials marketed under the tradename ZONYL® (DuPont Performance Chemicals). These include, for example, ZONYL® FSO and ZONYL® FSN. These compounds have the following formula:  $RfCH_2CH_2O(CH_2CH_2O)_xH$  where  $Rf$  is  $F(CF_2CF_2)_y$ . For ZONYL® FSO,  $x$  is 0 to about 15 and  $y$  is 1 to about 7. For ZONYL® FSN,  $x$  is 0 to about 25 and  $y$  is 1 to about 9.

[0062] An example of a suitable cationic fluorosurfactant compound has the following structure:  $C_nF_{2n+1}SO_2NHC_3H_6N^+(CH_3)_3I^-$  where  $n \sim 8$ . This cationic fluorosurfactant is available under the tradename Fluorad® FC-135 from 3M. Another example of a suitable cationic fluorosurfactant is  $F_3-(CF_2)_n-(CH_2)_mSCH_2CHOH-CH_2-N^+R_1R_2R_3Cl^-$  wherein:  $n$  is 5-9 and  $m$  is 2, and  $R_1$ ,  $R_2$  and  $R_3$  are  $-CH_3$ . This cationic fluorosurfactant is available under the tradename ZONYL® FSD (available from DuPont, described as 2-hydroxy-3-((gamma-omega-perfluoro-  $C_{6-20}$ -alkyl)thio)-N,N,N-trimethyl-1-propyl ammonium chloride). Other cationic fluorosurfactants suitable for use in the present invention are also described in EP 866,115 to Leach and Niwata.

[0063] The fluorosurfactant selected from the group of nonionic fluorosurfactant, cationic fluorosurfactant, and mixtures thereof may be present in amounts of from 0.001 to 5% wt., preferably from 0.01 to 1% wt., and more preferably from 0.01 to 0.5% wt.

#### Solvent

[0064] Compositions for use herein may contain volatile solvents. As used herein, "volatile" refers to substances with a significant amount of vapour pressure under ambient conditions, as is understood by those in the art. The volatile solvents for use herein will suitably have a vapour pressure of about 2 kPa or more, or about 6 kPa or more at 25° C. The volatile solvents for use herein will suitably have a boiling point under 1 atm, of less than about 150° C., or less than about 100° C., or less than about 90° C., or less than about 80° C.

[0065] The volatile solvents for use herein may be safe for use on a wide range of substrates, more preferably on human or animal skin or hair. Suitable volatile solvents include, but are not limited to, those found in the *CTFA International Cosmetic Ingredient Dictionary and Handbook*, 7th edition, volume 2 P1670-1672, edited by Wenninger and McEwen (The Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D.C., 1997). Conventionally used volatile solvents include C3-C14 saturated and unsaturated, straight or branched chain hydrocarbons such as cyclohexane, hexane, heptane, isooctane, isopentane, pentane, toluene, xylene; halogenated alkanes such as perfluorodecalin; ethers such as dimethyl ether, diethyl ether; straight or branched chain alcohols and diols such as methanol, ethanol, propanol, isopropanol, n-butyl alcohol, t-butyl alcohol, benzyl alcohol, butoxypropanol, butylene glycol, isopentyldiol; aldehydes and ketones such as acetone;



volatile silicones such as cyclomethicones for example octamethyl cyclo tetrasiloxane and decamethyl cyclopentane siloxane; volatile siloxanes such as phenyl pentamethyl disiloxane, phenylethylpentamethyl disiloxane, hexamethyl disiloxane, methoxy propylheptamethyl cyclotetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl pentamethyl disiloxane, octamethyl cyclotetrasiloxane, decamethyl cyclopentasiloxane; propellants, and mixtures thereof. Suitable volatile solvents are ethers such as dimethyl ether, diethyl ether; straight or branched chain alcohols and diols such as methanol, ethanol, propanol, isopropanol, n- butyl alcohol, t-butyl alcohol, benzyl alcohol, butoxypropanol, butylene glycol, isopentyldiol; volatile silicones such as cyclomethicones for example octamethyl cyclo tetrasiloxane and decamethyl cyclopentane siloxane; propellants, and mixtures thereof. Suitable for use herein are C1-C4 straight chain or branched chain alcohols for example methanol, ethanol, propanol, isopropanol and butanol and mixtures thereof.

[0066] Suitable organic solvents include, but are not limited to, C<sub>1-6</sub> alkanols, C<sub>1-6</sub> diols, C<sub>1-10</sub> alkyl ethers of alkylene glycols, C<sub>3-24</sub> alkylene glycol ethers, polyalkylene glycols, short chain carboxylic acids, short chain esters, isoparafinic hydrocarbons, mineral spirits, alkylaromatics, terpenes, terpene derivatives, terpenoids, terpenoid derivatives, formaldehyde, and pyrrolidones. Alkanols include, but are not limited to, methanol, ethanol, n-propanol, isopropanol, butanol, pentanol, and hexanol, and isomers thereof. Diols include, but are not limited to, methylene, ethylene, propylene and butylene glycols. Alkylene glycol ethers include, but are not limited to, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, ethylene glycol monohexyl ether, diethylene glycol monopropyl ether, diethylene glycol monobutyl ether, diethylene glycol monohexyl ether, propylene glycol methyl ether, propylene glycol ethyl ether, propylene glycol n-propyl ether, propylene glycol monobutyl ether, propylene glycol t-butyl ether, di- or tri-polypropylene glycol methyl or ethyl or propyl or butyl ether, acetate and propionate esters of glycol ethers. Short chain carboxylic acids include, but are not limited to, acetic acid, glycolic acid, lactic acid and propionic acid. Short chain esters include, but are not limited to, glycol acetate, and cyclic or linear volatile methylsiloxanes. Water insoluble solvents such as isoparafinic hydrocarbons, mineral spirits, alkylaromatics, terpenoids, terpenoid derivatives, terpenes, and terpenes derivatives can be mixed with a water soluble solvent when employed.

[0067] Examples of organic solvent having a vapor pressure less than 0.1 mm Hg (20° C) include, but are not limited to, dipropylene glycol n-propyl ether, dipropylene glycol t-butyl ether, dipropylene glycol n-butyl ether, tripropylene glycol methyl ether, tripropylene glycol n-butyl ether, diethylene glycol propyl ether, diethylene glycol butyl ether, dipropylene glycol methyl ether acetate, diethylene glycol ethyl ether acetate, and diethylene glycol butyl ether acetate (all available from ARCO Chemical Company).

[0068] While the compositions of the present invention must comprise a volatile solvent they may also comprise "nonvolatile" solvents. Suitable non-volatile solvents include, but are not limited to, benzyl benzoate, diethyl phthalate, isopropyl myristate, and mixtures thereof.

[0069] The solvents are present at a level of from about 0.001% to 30%, or from 0.01% to 20%, or from 1% to 10% by weight.

#### Surface Protectants

[0070] The cleaning compositions may contain "soil-resist agent", which resist or repel dirt, oil, or other substances not normally intended to be present on a substrate such as a textile material. Fluorochemical soil-resist agents may include polymers or compounds having pendent or end groups of perfluoroalkyl moieties, fluorosurfactants, or fluoro-intermediates. Examples of some suitable fluorochemical soil-resist agents include Zonyl® 7950 and Zonyl® 5180 (available from DuPont).

[0071] The cleaning compositions may contain "stain-resist agent", which impart partial or total resistance to staining. Staining is defined as discoloration due to a material adding color (such as food or liquid) that exhibits resistance to removal by standard cleaning methods. Stain-resist agents may include compounds such as hydrolyzed maleic anhydride co- or terpolymers with aliphatic alpha olefins, aromatic olefins or vinyl ethers, and homo- or copolymers of methacrylic acid. One stain-resist agent is Zelan 338, which is available from DuPont.

[0072] The surface protectant of the present invention may contribute to both the oil and water repellency, provide gloss to the cleaned carpet, and maximize the anti-resoiling features of the compositions of the present invention. In addition, the surface protectant

component may assist in solubilizing relatively insoluble ingredients, thus assisting in the formation of a carpet cleaning product having integrated properties.

[0073] The surface protectant of the present invention may be an olefinic/acrylic polymer. Olefinic/acrylic polymers comprise a combination of alpha, beta unsaturated carboxylated monomers, and olefinic monomers such as styrene, alpha methyl styrene or blocked alpha, beta unsaturated esterified carboxylates or amides. The carboxylated polymer may be an ammonium or sodium salt. The polymer may be dissolved into water with an alkali to form a polymer having an acid number (AN) of 10 to 450, or from 20 to 350.

[0074] The surface protectants may be olefinic/acrylic solutions having 60% styrene/AMS/acrylic resin, having a molecular weight ("Mw") 1,700, a glass transition temperature ("Tg") of 56°, and AN of 238; 34% styrene/AMS/acrylic resin, Mw 8,500, Tg of 85° C, AN of 215; 30.5% styrene/AMS/acrylic resin, Mw 12,500, Tg of 73° C, AN of 213; and olefinic/acrylic polymer emulsions such as 45.5% styrene/AMS/2-ethyl hexylacrylate/acrylic acid ("AA"), Mw >200,000, Tg of 7° C, AN of 50; 45% styrene/AMS/AA/methyl methacrylate ("MMA")/butyl methacrylate ("BMA") /butyl acrylate, Mw >200,000, Tg of 64° C, AN of 53; and about 98% solid styrene and AMS/acrylic resin which is cut into solution with 28% ammonia to pH of 7.85, Mw 17,000, Tg of 85° C, and AN of 175. One example is Zelan 338 (30% Carboxylated Polymer, AN196)

[0075] The surface protectant, which can include the stainblocking polymers, is generally present in an amount from about 0.1% to 7.0%, or from 1.0% to 4.0%, or from 0.5% to 3.5% by weight of the compositions of the present invention.

#### Additional adjuncts

[0076] The cleaning compositions optionally contain one or more of the following adjuncts: stain and soil repellants, lubricants, odor control agents, perfumes, fragrances and fragrance release agents, and bleaching agents. Other adjuncts include, but are not limited to, acids, electrolytes, dyes and/or colorants, solubilizing materials, stabilizers, thickeners, defoamers, hydrotropes, cloud point modifiers, preservatives, and other polymers. Other adjuncts include, but are not limited to corrosion control agents, color protection agents, allergen & insect control, brighteners, film formers, thickeners, spray

modifiers, and salts or antifoam agents to control foam break properties. The solubilizing materials, when used, include, but are not limited to, hydrotropes (e.g. water soluble salts of low molecular weight organic acids such as the sodium and/or potassium salts of toluene, cumene, and xylene sulfonic acid). The acids, when used, include, but are not limited to, organic hydroxy acids, citric acids, keto acid, and the like. Electrolytes, when used, include, calcium, sodium and potassium chloride. Thickeners, when used, include, but are not limited to, polyacrylic acid, xanthan gum, calcium carbonate, aluminum oxide, alginates, guar gum, methyl, ethyl, clays, and/or propyl hydroxycelluloses. Defoamers, when used, include, but are not limited to, silicones, aminosilicones, silicone blends, and/or silicone/ hydrocarbon blends. Bleaching agents, when used, include, but are not limited to, peracids, hypohalite sources, hydrogen peroxide, and/or sources of hydrogen peroxide.

[0077] Preservatives, when used, include, but are not limited to, mildewstat or bacteriostat, methyl, ethyl and propyl parabens, short chain organic acids (e.g. acetic, lactic and/or glycolic acids), bisguanidine compounds (e.g. Dantagard and/or Glydant) and/or short chain alcohols (e.g. ethanol and/or IPA). The mildewstat or bacteriostat includes, but is not limited to, mildewstats (including non-isothiazolone compounds) include Kathon GC, a 5-chloro-2-methyl-4-isothiazolin-3-one, KATHON ICP, a 2-methyl-4-isothiazolin-3-one, and a blend thereof, and KATHON 886, a 5-chloro-2-methyl-4-isothiazolin-3-one, all available from Rohm and Haas Company; BRONOPOL, a 2-bromo-2-nitropropane 1, 3 diol, from Boots Company Ltd., PROXEL CRL, a propyl-p-hydroxybenzoate, from ICI PLC; NIPASOL M, an o-phenyl-phenol, Na<sup>+</sup> salt, from Nipa Laboratories Ltd., DOWICIDE A, a 1,2-Benzoisothiazolin-3-one, from Dow Chemical Co., and IRGASAN DP 200, a 2,4,4'-trichloro-2-hydroxydiphenylether, from Ciba-Geigy A.G.

#### Antimicrobial Agent

[0078] Antimicrobial agents include quaternary ammonium compounds and phenolics. Non-limiting examples of these quaternary compounds include benzalkonium chlorides and/or substituted benzalkonium chlorides, di(C<sub>6</sub>- C<sub>14</sub>)alkyl di short chain (C<sub>1-4</sub> alkyl and/or hydroxyalkyl) quaternary ammonium salts, N-(3-chloroallyl) hexaminium chlorides, benzethonium chloride, methylbenzethonium chloride, and cetylpyridinium chloride.

Other quaternary compounds include the group consisting of dialkyldimethyl ammonium chlorides, alkyl dimethylbenzylammonium chlorides, dialkylmethylbenzylammonium chlorides, and mixtures thereof. Biguanide antimicrobial actives including, but not limited to polyhexamethylene biguanide hydrochloride, p-chlorophenyl biguanide; 4-chlorobenzhydryl biguanide, halogenated hexidine such as, but not limited to, chlorhexidine (1,1'-hexamethylene -bis-5-(4-chlorophenyl biguanide) and its salts are also in this class.

**[0079]** Specific examples of phenol derivatives include, but are not limited to, chlorophenols (o-, m-, p-), 2,4-dichlorophenol, p-nitrophenol, picric acid, xlenol, p-chloro-m-xlenol, cresols (o-, m-, p-), p-chloro-m- cresol, pyrocatechol, resorcinol, 4-n-hexylresorcinol, pyrogallol, phloroglucin, carvacrol, thymol, p-chlorothymol, o-phenylphenol, o- benzylphenol, p-chloro-o-benzylphenol, phenol, 4-ethylphenol, and 4-phenolsulfonic acid. Other phenol derivatives are listed in WO 98/55096 and U.S. Pat. No. 6,113,933, incorporated herein by reference.

#### Builder/Buffer

**[0080]** The cleaning composition may include a builder or buffer, which increase the effectiveness of the surfactant or improve aerosol corrosion control. The builder or buffer can also function as a softener and/or a sequestering agent in the cleaning composition. A variety of builders or buffers can be used and they include, but are not limited to, phosphate-silicate compounds, zeolites, alkali metal, ammonium and substituted ammonium polyacetates, trialkali salts of nitrilotriacetic acid, carboxylates, polycarboxylates, carbonates, bicarbonates, polyphosphates, aminopolycarboxylates, polyhydroxysulfonates, and starch derivatives.

**[0081]** Builders or buffers can also include polyacetates and polycarboxylates. The polyacetate and polycarboxylate compounds include, but are not limited to, sodium, potassium, lithium, ammonium, and substituted ammonium salts of ethylenediamine tetraacetic acid, ethylenediamine triacetic acid, ethylenediamine tetrapropionic acid, diethylenetriamine pentaacetic acid, nitrilotriacetic acid, oxydisuccinic acid, iminodisuccinic acid, mellitic acid, polyacrylic acid or polymethacrylic acid and copolymers, benzene polycarboxylic acids, gluconic acid, sulfamic acid, oxalic acid,

phosphoric acid, phosphonic acid, organic phosphonic acids, acetic acid, and citric acid. These builders or buffers can also exist either partially or totally in the hydrogen ion form.

**[0082]** The builder agent can include sodium and/or potassium salts of EDTA and substituted ammonium salts. The substituted ammonium salts include, but are not limited to, ammonium salts of methylamine, dimethylamine, butylamine, butylenediamine, propylamine, triethylamine, trimethylamine, monoethanolamine, diethanolamine, triethanolamine, isopropanolamine, ethylenediamine tetraacetic acid and propanolamine.

**[0083]** Buffering and pH adjusting agents, when used, include, but are not limited to, organic acids, mineral acids, alkali metal and alkaline earth salts of silicate, metasilicate, polysilicate, borate, hydroxide, carbonate, carbamate, phosphate, polyphosphate, pyrophosphates, triphosphates, tetraphosphates, ammonia, hydroxide, monoethanolamine, monopropanolamine, diethanolamine, dipropanolamine, triethanolamine, and 2-amino-2-methylpropanol. Preferred buffering agents for compositions of this invention are nitrogen-containing materials. Some examples are amino acids such as lysine or lower alcohol amines like mono-, di-, and tri-ethanolamine. Other preferred nitrogen-containing buffering agents are tri(hydroxymethyl) amino methane (TRIS), 2-amino-2-ethyl-1,3-propanediol, 2-amino-2-methyl- propanol, 2- amino-2-methyl-1,3-propanol, disodium glutamate, N-methyl diethanolarnide, 2-dimethylamino- 2-methylpropanol (DMAMP), 1,3-bis(methylamine)-cyclohexane, 1,3-diamino-propanol N,N'- tetra-methyl-1,3-diamino-2-propanol, N,N-bis(2-hydroxyethyl)glycine (bicine) and N-tris(hydroxymethyl)methyl glycine (tricine). Other suitable buffers include ammonium carbamate, citric acid, acetic acid. Mixtures of any of the above are also acceptable. Useful inorganic buffers/alkalinity sources include ammonia, the alkali metal carbonates and alkali metal phosphates, e.g., sodium carbonate, sodium polyphosphate. For additional buffers see WO 95/07971, which is incorporated herein by reference. Other preferred pH adjusting agents include sodium or potassium hydroxide.

**[0084]** When employed, the builder, buffer, or pH adjusting agent comprises at least about 0.001% and typically about 0.01-5% of the cleaning composition. The builder or buffer content may be about 0.01-2%.

### Pine oil, terpene derivatives and essential oils

[0085] Compositions according to the invention may comprise pine oil, terpene derivatives and/or essential oils. Pine oil, terpene derivatives and essential oils are used primarily for cleaning efficacy. They may also provide some antimicrobial efficacy and deodorizing properties. Pine oil, terpene derivatives and essential oils may be present in the compositions in amounts of up to about 1% by weight, preferably in amounts of 0.01% to 0.5% by weight.

[0086] Pine oil is a complex blend of oils, alcohols, acids, esters, aldehydes and other organic compounds. These include terpenes which include a large number of related alcohols or ketones. Some important constituents include terpineol. One type of pine oil, synthetic pine oil, will generally contain a higher content of turpentine alcohols than the two other grades of pine oil, namely steam distilled and sulfate pine oils. Other important compounds include alpha- and beta- pinene (turpentine), abietic acid (rosin), and other isoprene derivatives. Particularly effective pine oils are commercially available from Mellennium Chemicals, under the Glidco tradename. These pine oils vary in the amount of terpene alcohols and alpha-terpineol.

[0087] Terpene derivatives appropriate for use in the inventive composition include terpene hydrocarbons having a functional group, such as terpene alcohols, terpene ethers, terpene esters, terpene aldehydes and terpene ketones. Examples of suitable terpene alcohols include verbenol, transpinocarveol, cis-2-pinanol, nopol, isoborneol, carbeol, piperitol, thymol, alpha-terpineol, terpinen-4-ol, menthol, 1,8-terpin, dihydro-terpineol, nerol, geraniol, linalool, citronellol, hydroxycitronellol, 3, 7-dimethyl octanol, dihydro-myrcenol, tetrahydro-alloocimenol, perillalcohol, and faltarindiol. Examples of suitable terpene ether and terpene ester solvents include 1,8-cineole, 1,4-cineole, isobornyl methylether, rose pyran, menthofuran, trans-anethole, methyl chavicol, allocimene diepoxide, limonene mono-epoxide, isobornyl acetate, nonyl acetate, terpinyl acetate, linalyl acetate, geranyl acetate, citronellyl acetate, dihydro-terpinyl acetate and meryl acetate. Further, examples of suitable terpene aldehyde and terpene ketone solvents include myrtenal, campholenic aldehyde, perillaldehyde, citronellal, citral, hydroxy citronellal, camphor, verbenone, carvenone, dihydro-carvone, carvone, piperitone,

menthone, geranyl acetone, pseudo- ionone, ionine, iso-pseudo-methyl ionone, n-pseudo-methyl ionone, iso-methyl ionone and n-methyl ionone.

[0088] Essential oils include, but are not limited to, those obtained from thyme, lemongrass, citrus, lemons, oranges, anise, clove, aniseed, pine, cinnamon, geranium, roses, mint, lavender, citronella, eucalyptus, peppermint, camphor, sandalwood, rosmarin, vervain, fleagrass, lemongrass, ratanhia, cedar and mixtures thereof. Preferred essential oils to be used herein are thyme oil, clove oil, cinnamon oil, geranium oil, eucalyptus oil, peppermint oil, mint oil or mixtures thereof.

[0089] Actives of essential oils to be used herein include, but are not limited to, thymol (present for example in thyme), eugenol (present for example in cinnamon and clove), menthol (present for example in mint), geraniol (present for example in geranium and rose), verbenone (present for example in vervain), eucalyptol and pinocarvone (present in eucalyptus), cedrol (present for example in cedar), anethol (present for example in anise), carvacrol, hinokitiol, berberine, ferulic acid, cinnamic acid, methyl salicylic acid, methyl salicylate, terpineol and mixtures thereof. Suitable actives of essential oils to be used herein are thymol, eugenol, verbenone, eucalyptol, terpineol, cinnamic acid, methyl salicylic acid, citric acid and/or geraniol.

[0090] Other essential oils include Anethole 20/21 natural, Aniseed oil china star, Aniseed oil globe brand, Balsam (Peru), Basil oil (India), Black pepper oil, Black pepper oleoresin 40/20, Bois de Rose (Brazil) FOB, Borneol Flakes (China), Camphor oil, White, Camphor powder synthetic technical, Canaga oil (Java), Cardamom oil, Cassia oil (China), Cedarwood oil (China) BP, Cinnamon bark oil, Cinnamon leaf oil, Citronella oil, Clove bud oil, Clove leaf, Coriander (Russia), Coumarin 69.degree. C. (China), Cyclamen Aldehyde, Diphenyl oxide, Ethyl vanilin, Eucalyptol, Eucalyptus oil, Eucalyptus citriodora, Fennel oil, Geranium oil, Ginger oil, Ginger oleoresin (India), White grapefruit oil, Guaiacwood oil, Gurjun balsam, Heliotropin, Isobomyl acetate, Isolongifolene, Juniper berry oil, L-methhyl acetate, Lavender oil, Lemon oil, Lemongrass oil, Lime oil distilled, Litsea Cubeba oil, Longifolene, Menthol crystals, Methyl cedryl ketone, Methyl chavicol, Methyl salicylate, Musk ambrette, Musk ketone, Musk xylol, Nutmeg oil, Orange oil, Patchouli oil, Peppermint oil, Phenyl ethyl alcohol, Pimento berry oil, Pimento leaf oil, Rosalin, Sandalwood oil, Sandenol, Sage oil, Clary sage, Sassafras oil, Spearmint



oil, Spike lavender, Tagetes, Tea tree oil, Vanilin, Vetyver oil (Java), Wintergreen. Each of these botanical oils is commercially available.

[0091] Suitable oils include peppermint oil, lavender oil, bergamot oil (Italian), rosemary oil (Tunisian), and sweet orange oil. These may be commercially obtained from a variety of suppliers including: Givadan Roure Corp. (Clifton, N.J.); Berje Inc. (Bloomfield, N.J.); BBA Aroma Chemical Div. of Union Camp Corp. (Wayne, N.J.); Firmenich Inc. (Plainsboro N.J.); Quest International Fragrances Inc. (Mt. Olive Township, N.J.); Robertet Fragrances Inc. (Oakland, N.J.).

[0092] Suitable lemon oil and d-limonene compositions which are useful in the invention include mixtures of terpene hydrocarbons obtained from the essence of oranges, e.g., cold-pressed orange terpenes and orange terpene oil phase ex fruit juice, and the mixture of terpene hydrocarbons expressed from lemons and grapefruit.

#### Polymers

[0093] In suitable embodiments of the invention, polymeric material that improves the hydrophilicity of the surface being treated is incorporated into the present compositions. The increase in hydrophilicity provides improved final appearance by providing "sheeting" of the water from the surface and/or spreading of the water on the surface, and this effect is preferably seen when the surface is rewetted and even when subsequently dried after the rewetting. Polymer substantivity is beneficial as it prolongs the sheeting and cleaning benefits. Another important feature of preferred polymers is lack of visible residue upon drying. In suitable embodiments, the polymer comprises from about 0.001 to 5%, or from 0.01 to 1%, or from 0.1 to 0.5% of the cleaning composition.

[0094] In general, the aqueous polymer containing composition may comprise a water soluble or water dispersible polymer. The hydrophilic polymers preferably are attracted to surfaces and are absorbed thereto without covalent bonds. Examples of suitable polymers include the polymers and co-polymers of N,N dimethyl acrylamide, acrylamide, and certain monomers containing quaternary ammonium groups or amphoteric groups that favor substantivity to surfaces, along with co-monomers that favor adsorption of water, such as, for example, acrylic acid and other acrylate salts, sulfonates, betaines, and ethylene oxides.

[0095] With respect to the synthesis of the water soluble or water dispersible cationic copolymer, the level of the first monomer, which has a permanent cationic charge or that is capable of forming a cationic charge on protonation, is typically between 3 and 80 mol% and preferably 10 to 60 mol% of the copolymer. The level of second monomer, which is an acidic monomer that is capable of forming an anionic charge in the composition, when present is typically between 3 and 80 mol% and preferably 10 to 60 mol% of the copolymer. The level of the third monomer, which has an uncharged hydrophilic group, when present is typically between 3 and 80 mol% and preferably 10 to 60 mol% of the copolymer. When present, the level of uncharged hydrophobic monomer is less than about 50 mol% and preferably less than 10 mol% of the copolymer. The molar ratio of the first monomer to the second monomer typically ranges from 19:1 to 1:10 and preferably ranges from 9:1 to 1:6. The molar ratio of the first monomer to the third monomer is typically ranges from 4:1 to 1:4 and preferably ranges from 2:1 to 1:2.

[0096] The average molecular weight of the copolymer typically ranges from about 5,000 to about 10,000,000, with the preferred molecular weight range depending on the polymer composition with the proviso that the molecular weight is selected so that the copolymer is water soluble or water dispersible to at least 0.01% by weight in distilled water at 25°C.

[0097] Examples of permanently cationic monomers include, but are not limited to, quaternary ammonium salts of substituted acrylamide, methacrylamide, acrylate and methacrylate, such as trimethylammoniummethylemethacrylate, trimethylammoniumpropylmethacrylamide, trimethylammoniummethylemethacrylate, trimethylammoniumpropylacrylamide, 2-vinyl N-alkyl quaternary pyridinium, 4-vinyl N-alkyl quaternary pyridinium, 4-vinylbenzyltrialkylammonium, 2-vinyl piperidinium, 4-vinyl piperidinium, 3-alkyl 1-vinyl imidazolium, diallyldimethylammonium, and the ionene class of internal cationic monomers as described by D. R. Berger in *Cationic Surfactants, Organic Chemistry*, edited by J. M. Richmond, Marcel Dekker, New York, 1990, ISBN 0-8247-8381-6, which is incorporated herein by reference. This class includes co-poly ethylene imine, co-poly ethoxylated ethylene imine and co-poly quaternized ethoxylated ethylene imine, co-poly [(dimethylimino) trimethylene (dimethylimino) hexamethylene disalt], co-poly [(diethylimino) trimethylene (dimethylimino) trimethylene disalt], co-poly [(dimethylimino) 2-hydroxypropyl salt], co-polyquarternium-2, co-polyquarternium-17, and co-polyquarternium-18, as described in

the *International Cosmetic Ingredient Dictionary*, 5th Edition, edited by J. A. Wenninger and G. N. McEwen, which is incorporated herein by reference. Other cationic monomers include those containing cationic sulfonium salts such as co-poly-1-[3-methyl-4-(vinylbenzyloxy)phenyl] tetrahydrothiophenium chloride. Especially preferred monomers are mono- and di-quaternary derivatives of methacrylamide. The counterion of the cationic co-monomer can be selected from, for example, chloride, bromide, iodide, hydroxide, phosphate, sulfate, hydrosulfate, ethyl sulfate, methyl sulfate, formate, and acetate.

[0098] Examples of monomers that are cationic on protonation include, but are not limited to, acrylamide, N,N-dimethylacrylamide, N,N di-isopropylacrylamide, N-vinylimidazole, N-vinylpyrrolidone, ethyleneimine, dimethylaminohydroxypropyl diethylenetriamine, dimethylaminoethylmethacrylate, dimethylaminopropylmethacrylamide, dimethylaminoethylacrylate, dimethylaminopropylacrylamide, 2-vinyl pyridine, 4-vinyl pyridine, 2-vinyl piperidine, 4-vinylpiperidine, vinyl amine, diallylamine, methyldiallylamine, vinyl oxazolidone; vinyl methyloxazolidone, and vinyl caprolactam.

[0099] Monomers that are cationic on protonation typically contain a positive charge over a portion of the pH range of 2-11. Such suitable monomers are also presented in *Water-Soluble Synthetic Polymers: Properties and Behavior*, Volume II, by P. Molyneux, CRC Press, Boca Raton, 1983, ISBN 0-8493-6136. Additional monomers can be found in the *International Cosmetic Ingredient Dictionary*, 5th Edition, edited by J. A. Wenninger and G. N. McEwen, The Cosmetic, Toiletry, and Fragrance Association, Washington D.C., 1993, ISBN 1-882621-06-9. A third source of such monomers can be found in *Encyclopedia of Polymers and Thickeners for Cosmetics*, by R. Y. Lochhead and W. R. Fron, Cosmetics & Toiletries, vol. 108, May 1993, pp 95-135. All three references are incorporated herein.

[00100] Examples of acidic monomers that are capable of forming an anionic charge in the composition include, but are not limited to, acrylic acid, methacrylic acid, ethacrylic acid, dimethylacrylic acid, maleic anhydride, succinic anhydride, vinylsulfonate, cyanoacrylic acid, methylenemalononic acid, vinylacetic acid, allylacetic acid, ethylideneacetic acid, propylideneacetic acid, crotonic acid, fumaric acid, itaconic acid, sorbic acid, angelic acid, cinnamic acid, styrylacrylic acid, citraconic acid, glutaconic acid, aconitic acid, phenylacrylic acid, acryloxypropionic acid, citraconic acid,

vinylbenzoic acid, N- vinylsuccinamidic acid, mesaconic acid, methacroylalanine, acryloylhydroxyglycine, sulfoethyl methacrylate, sulfopropyl acrylate, and sulfoethyl acrylate. Preferred acid monomers also include styrenesulfonic acid, 2-methacryloyloxymethane-1-sulfonic acid, 3- methacryloyloxypropane-1- sulfonic acid, 3-(vinylloxy)propane-1-sulfonic acid, ethylenesulfonic acid, vinyl sulfuric acid, 4-vinylphenyl sulfuric acid, ethylene phosphonic acid and vinyl phosphoric acid. Most preferred monomers include acrylic acid, methacrylic acid and maleic acid. The copolymers useful in this invention may contain the above acidic monomers and the alkali metal, alkaline earth metal, and ammonium salts thereof.

**[00101]** Examples of monomers having an uncharged hydrophilic group include but are not limited to vinyl alcohol, vinyl acetate, vinyl methyl ether, vinyl ethyl ether, ethylene oxide and propylene oxide. Especially preferred are hydrophilic esters of monomers, such as hydroxyalkyl acrylate esters, alcohol ethoxylate esters, alkylpolyglycoside esters, and polyethylene glycol esters of acrylic and methacrylic acid.

**[00102]** Finally, examples of uncharged hydrophobic monomers include, but are not limited to, C<sub>1</sub>-C<sub>4</sub> alkyl esters of acrylic acid and of methacrylic acid.

**[00103]** The copolymers are formed by copolymerizing the desired monomers. Conventional polymerization techniques can be employed. Illustrative techniques include, for example, solution, suspension, dispersion, or emulsion polymerization. A preferred method of preparation is by precipitation or inverse suspension polymerization of the copolymer from a polymerization media in which the monomers are dispersed in a suitable solvent. The monomers employed in preparing the copolymer are preferably water soluble and sufficiently soluble in the polymerization media to form a homogeneous solution. They readily undergo polymerization to form polymers which are water-dispersable or water-soluble. The preferred copolymers contain acrylamide, methacrylamide and substituted acrylamides and methacrylamides, acrylic and methacrylic acid and esters thereof. Suitable synthetic methods for these copolymers are described, for example, in Kirk-Othmer, *Encyclopedia of Chemical Technology*, Volume 1, Fourth Ed., John Wiley & Sons.

**[00104]** Other examples of polymers that provide the sheeting and anti-spotting benefits are polymers that contain amine oxide hydrophilic groups. Polymers that contain

other hydrophilic groups such a sulfonate, pyrrolidone, and/or carboxylate groups can also be used. Examples of desirable poly-sulfonate polymers include polyvinylsulfonate, and more preferably polystyrene sulfonate, such as those sold by Monomer-Polymer Dajac (1675 Bustleton Pike, Feasterville, Pa. 19053). A typical formula is as follows:  

$$[\text{CH}(\text{C}_6\text{H}_4\text{SO}_3\text{Na})-\text{CH}_2]_n-\text{CH}(\text{C}_6\text{H}_5)-\text{CH}_2$$
 wherein n is a number to give the appropriate molecular weight as disclosed below.

**[00105]** Typical molecular weights are from about 10,000 to about 1,000, 000, preferably from about 200,000 to about 700,000. Preferred polymers containing pyrrolidone functionalities include polyvinyl pyrrolidone, quaternized pyrrolidone derivatives (such as Gafquat 755N from International Specialty Products), and copolymers containing pyrrolidone, such as polyvinylpyrrolidone/dimethylaminoethylmethacrylate (available from ISP) and polyvinyl pyrrolidone/acrylate (available from BASF). Other materials can also provide substantivity and hydrophilicity including cationic materials that also contain hydrophilic groups and polymers that contain multiple ether linkages. Cationic materials include cationic sugar and/or starch derivatives and the typical block copolymer detergent surfactants based on mixtures of polypropylene oxide and ethylene oxide are representative of the polyether materials. The polyether materials are less substantive, however.

**[00106]** Preferred polymers comprise water-soluble amine oxide moieties. It is believed that the partial positive charge of the amine oxide group can act to adhere the polymer to the surface of the surface substrate, thus allowing water to "sheet" more readily. To the extent that polymer anchoring promotes better "sheeting" higher molecular materials are preferred. Increased molecular weight improves efficiency and effectiveness of the amine oxide-based polymer. The preferred polymers of this invention have one or more monomeric units containing at least one N-oxide group. At least about 10%, preferably more than about 50%, more preferably greater than about 90% of said monomers forming said polymers contain an amine oxide group. These polymers can be described by the general formula: P(B) wherein each P is selected from homopolymerizable and copolymerizable moieties which attach to form the polymer backbone, preferably vinyl moieties, e.g. C(R)<sub>2</sub>--C(R)<sub>2</sub>, wherein each R is H, C<sub>1</sub>-C<sub>12</sub> (preferably C<sub>sub.1</sub>-C<sub>sub.4</sub>) alkyl(ene), C<sub>6</sub>-C<sub>12</sub> aryl(ene) and/or B; B is a moiety selected from substituted and unsubstituted, linear and cyclic C<sub>1</sub>-C<sub>12</sub> alkyl, C<sub>1</sub>-C<sub>12</sub> alkylene, C<sub>1</sub>-

C12 heterocyclic, aromatic C6-C12 groups and wherein at least one of said B moieties has at least one amine oxide group present; u is from a number that will provide at least about 10% monomers containing an amine oxide group to about 90%; and t is a number such that the average molecular weight of the polymer is from about 2,000 to about 500,000, preferably from about 5,000 to about 250, 000, and more preferably from about 7,500 to about 200,000. Preferred polymers also include poly(4-vinylpyridine N-oxide) polymers (PVNO), wherein the average molecular weight of the polymer is from about 2,000 to about 500,000 preferably from about 5,000 to about 400,000, and more preferably from about 7,500 to about 300,000. In general, higher molecular weight polymers are preferred. Often, higher molecular weight polymers allow for use of lower levels of the wetting polymer, which can provide benefits in floor cleaner applications. The desirable molecular weight range of polymers useful in the present invention stands in contrast to that found in the art relating to polycarboxylate, polystyrene sulfonate, and polyether based additives, which prefer molecular weights in the range of 400,000 to 1,500,000. Lower molecular weights for the preferred poly-amine oxide polymers of the present invention are due to greater difficulty in manufacturing these polymers in higher molecular weight.

**[00107]** Some non-limiting examples of homopolymers and copolymers which can be used as water soluble polymers of the present invention are: adipic acid/dimethylaminohydroxypropyl diethylenetriamine copolymer; adipic acid/epoxypropyl diethylenetriamine copolymer; polyvinyl alcohol; methacryloyl ethyl betaine/methacrylates copolymer; ethyl acrylate/methyl methacrylate/methacrylic acid/acrylic acid copolymer; polyamine resins; and polyquaternary amine resins; poly(ethenylformamide); poly(vinylamine) hydrochloride; poly(vinyl alcohol-co-6% vinylamine); poly(vinyl alcohol- co-12% vinylamine); poly(vinyl alcohol-co-6% vinylamine hydrochloride); and poly(vinyl alcohol-co-12% vinylamine hydrochloride). Preferably, said copolymer and/or homopolymers are selected from the group consisting of adipic acid/dimethylaminohydroxypropyl diethylenetriamine copolymer; poly(vinylpyrrolidone/ dimethylaminoethyl methacrylate); polyvinyl alcohol; ethyl acrylate/methyl methacrylate/ethacrylic acid/acrylic acid copolymer; methacryloyl ethyl betaine/methacrylates copolymer; polyquaternary amine resins; poly(ethenylformamide); poly(vinylamine) hydrochloride; poly(vinyl alcohol-co-6% vinylamine); poly(vinyl

alcohol- co-12% vinylamine); poly(vinyl alcohol-co-6% vinylamine hydrochloride); and poly(vinyl alcohol-co-12% vinylamine hydrochloride).

**[00108]** Polymers useful in the present invention can be selected from the group consisting of copolymers of hydrophilic monomers. The polymer can be linear random or block copolymers, and mixtures thereof. The term "hydrophilic" is used herein consistent with its standard meaning of having affinity for water. As used herein in relation to monomer units and polymeric materials, including the copolymers, "hydrophilic" means substantially water soluble. In this regard, "substantially water soluble" shall refer to a material that is soluble in distilled (or equivalent) water, at 25° C., at a concentration of about 0.2% by weight, and are preferably soluble at about 1% by weight. The terms "soluble", "solubility" and the like, for purposes hereof, correspond to the maximum concentration of monomer or polymer, as applicable, that can dissolve in water or other solvents to form a homogeneous solution, as is well understood to those skilled in the art.

**[00109]** Nonlimiting examples of useful hydrophilic monomers are unsaturated organic mono- and polycarboxylic acids, such as acrylic acid, methacrylic acid, crotonic acid, maleic acid and its half esters, itaconic acid; unsaturated alcohols, such as vinyl alcohol, allyl alcohol; polar vinyl heterocyclics, such as, vinyl caprolactam, vinyl pyridine, vinyl imidazole; vinyl amine; vinyl sulfonate; unsaturated amides, such as acrylamides, e.g., N,N-dimethylacrylamide, N-t-butyl acrylamide; hydroxyethyl methacrylate; dimethylaminoethyl methacrylate; salts of acids and amines listed above; and the like; and mixtures thereof. Some preferred hydrophilic monomers are acrylic acid, methacrylic acid, N,N- dimethyl acrylamide, N,N-dimethyl methacrylamide, N-t-butyl acrylamide, dimethylamino ethyl methacrylate, thereof, and mixtures thereof.

**[00110]** Polycarboxylate polymers are those formed by polymerization of monomers, at least some of which contain carboxylic functionality. Common monomers include acrylic acid, maleic acid, ethylene, vinyl pyrrolidone, methacrylic acid, methacryloylethylbetaine, etc. Preferred polymers for substantivity are those having higher molecular weights. For example, polyacrylic acid having molecular weights below about 10,000 are not particularly substantive and therefore do not normally provide hydrophilicity for three rewettings with all compositions, although with higher levels and/or certain surfactants like amphoteric and/or zwitterionic detergent surfactants,

molecular weights down to about 1000 can provide some results. In general, the polymers should have molecular weights of more than about 10,000, preferably more than about 20,000, more preferably more than about 300,000, and even more preferably more than about 400,000. It has also been found that higher molecular weight polymers, e.g., those having molecular weights of more than about 3,000, 000, are extremely difficult to formulate and are less effective in providing anti-spotting benefits than lower molecular weight polymers. Accordingly, the molecular weight should normally be, especially for polyacrylates, from about 20,000 to about 3,000,000; preferably from about 20,000 to about 2,500,000; more preferably from about 300,000 to about 2,000,000; and even more preferably from about 400,000 to about 1, 500,000.

**[00111]** Non limiting examples of polymers for use in the present invention include the following: poly(vinyl pyrrolidone/acrylic acid) sold under the name "Acrylidone"® by ISP and poly(acrylic acid) sold under the name "Accumer"® by Rohm & Haas. Other suitable materials include sulfonated polystyrene polymers sold under the name Versaflex® sold by National Starch and Chemical Company, especially Versaflex 7000. The level of polymeric material will normally be less than about 0.5%, preferably from about 0.001% to about 0.4%, more preferably from about 0.01% to about 0.3%. In general, lower molecular weight materials such as lower molecular weight poly(acrylic acid), e.g., those having molecular weights below about 10,000, and especially about 2,000, do not provide good anti-spotting benefits upon rewetting, especially at the lower levels, e.g., about 0.02%. One should use only the more effective materials at the lower levels. In order to use lower molecular weight materials, substantivity should be increased, e.g., by adding groups that provide improved attachment to the surface, such as cationic groups, or the materials should be used at higher levels, e.g., more than about 0.05%.

#### Nanoparticles

**[00112]** Nanoparticles, defined as particles with diameters of about 400 nm or less, are technologically significant, since they are utilized to fabricate structures, coatings, and devices that have novel and useful properties due to the very small dimensions of their particulate constituents. "Non-photoactive" nanoparticles do not use UV or visible light to produce the desired effects. Nanoparticles can have many different particle shapes.



Shapes of nanoparticles can include, but are not limited to spherical, parallelepiped-shaped, tube shaped, and disc or plate shaped.

**[00113]** Nanoparticles with particle sizes ranging from about 2 nm to about 400 nm can be economically produced. Particle size distributions of the nanoparticles may fall anywhere within the range from about 1 nm, or less, to less than about 400 nm, alternatively from about 2 nm to less than about 100 nm, and alternatively from about 2 nm to less than about 50 nm. For example, a layer synthetic silicate can have a mean particle size of about 25 nanometers while its particle size distribution can generally vary between about 10 nm to about 40 nm. Alternatively, nanoparticles can also include crystalline or amorphous particles with a particle size from about 1, or less, to about 100 nanometers, alternatively from about 2 to about 50 nanometers. Nanotubes can include structures up to 1 centimeter long, alternatively with a particle size from about 1 nanometer, or less, to about 50 nanometers. Nanoparticles can be present from 0.01 to 1%.

**[00114]** Inorganic nanoparticles generally exist as oxides, silicates, carbonates and hydroxides. These nanoparticles are generally hydrophilic. Some layered clay minerals and inorganic metal oxides can be examples of nanoparticles. The layered clay minerals suitable for use in the coating composition include those in the geological classes of the smectites, the kaolins, the illites, the chlorites, the attapulgites and the mixed layer clays. Smectites include montmorillonite, bentonite, pyrophyllite, hectorite, saponite, sauconite, nontronite, talc, beidellite, volchonskoite and vermiculite. Kaolins include kaolinite, dickite, nacrite, antigorite, anauxite, halloysite, indellite and chrysotile. Illites include bravaisite, muscovite, paragonite, phlogopite and biotite. Chlorites include corrensite, penninite, donbassite, sudoite, pennine and clinocllore. Attapulgites include sepiolite and polygorskyte. Mixed layer clays include alleverdite and vermiculitebiotite. Variants and isomorphic substitutions of these layered clay minerals offer unique applications.

**[00115]** The layered clay minerals suitable for use in the coating composition may be either naturally occurring or synthetic. An example of one embodiment of the coating composition uses natural or synthetic hectorites, montmorillonites and bentonites. Another embodiment uses the hectorites clays commercially available. Typical sources of commercial hectorites are LAPONITE® from Southern Clay Products, Inc., U.S.A;

Veegum Pro and Veegum F from R. T. Vanderbilt, U.S.A.; and the Barasymms, Macaloids and Propaloids from Baroid Division, National Read Comp., U.S.A.

**[00116]** The inorganic metal oxides used in the coating composition may be silica- or alumina-based nanoparticles that are naturally occurring or synthetic. Aluminum can be found in many naturally occurring sources, such as kaolinite and bauxite. The naturally occurring sources of alumina are processed by the Hall process or the Bayer process to yield the desired alumina type required. Various forms of alumina are commercially available in the form of Gibbsite, Diaspore, and Boehmite from manufacturers such as Condea.

**[00117]** Synthetic hectorites, such as LAPONITE RD®, do not contain any fluorine. An isomorphous substitution of the hydroxyl group with fluorine will produce synthetic clays referred to as sodium magnesium lithium fluorosilicates. These sodium magnesium lithium fluorosilicates, marketed as LAPONITE B® and LAPONITE S®, contain fluoride ions of greater than 0% up to about 8%, and preferably about 6% by weight. LAPONITE B® particles are flat disc-shaped, or plate shaped, and have a mean particle size of about 40 nanometers in diameter and about 1 nanometer in thickness. Another variant, called LAPONITE S®, contains about 6% of tetrasodium polyphosphate as an additive. In some instances, LAPONITE B® by itself is believed, without wishing to be bound to any particular theory, to be capable of providing a more uniform coating (that is, more continuous, i. e., less openings in the way the coating forms after drying), and can provide a more substantive (or durable) coating than some of the other grades of LAPONITE® by themselves (such as LAPONITE RD®).

**[00118]** The aspect ratio for disk shaped nanoparticles is the ratio of the diameter of the clay particle to that of the thickness of the clay particle. The aspect ratio of individual particles of LAPONITE® B is approximately 40 and the aspect ratio of individual particles of LAPONITE® RD is approximately 25. A high aspect ratio is desirable for film formation of nanosized clay materials. More important to the invention is the aspect ratio of the dispersed particles in a suitable carrier medium, such as water. The aspect ratio of the particles in a dispersed medium can be considered to be lower where several of the disc shaped particles are stacked on top of one another than in the case of individual

particles. The aspect ratio of dispersions can be adequately characterized by TEM (transmission electron microscopy).

**[00119]** LAPONITE B® occurs in dispersions as essentially single clay particles or stacks of two or fewer clay particles. The LAPONITE RD® occurs essentially as stacks of two or more single clay particles. Thus, the aspect ratio of the particles dispersed in the carrier medium can be dramatically different from the aspect ratio of single disc-shaped particle. The aspect ratio of LAPONITE B® is about 20-40 and the aspect ratio of LAPONITE RD® is less than 15.

**[00120]** In some preferred embodiments, the nanoparticles will have a net excess charge on one of their dimensions. For instance, flat plate-shaped nanoparticles may have a positive charge on their flat surfaces, and a negative charge on their edges. Alternatively, such flat plate-shaped nanoparticles may have a negative charge on their flat surfaces and a positive charge on their edges. Preferably, the nanoparticles have an overall net negative charge. This is believed to aid in hydrophilizing the surface coated with the nanoparticles. The amount of charge, or "charge density", on the nanoparticles can be measured in terms of the mole ratio of magnesium oxide to lithium oxide in the nanoparticles. In preferred embodiments, the nanoparticles have a mole ratio of magnesium oxide to lithium oxide of less than or equal to about 11%.

**[00121]** Depending upon the application, the use of variants and isomorphous substitutions of LAPONITE® provides great flexibility in engineering the desired properties of the coating composition used in the present invention. The individual platelets of LAPONITE® are negatively charged on their faces and possess a high concentration of surface bound water. When applied to a hard surface, the hard surface is hydrophilically modified and exhibits surprising and significantly improved wetting and sheeting, quick drying, uniform drying, anti-spotting, anti-soil deposition, cleaner appearance, enhanced gloss, enhanced color, minor surface defect repair, improved smoothness, anti-hazing properties, modification of surface friction, reduced damage to abrasion and improved transparency properties. In addition, the LAPONITE® modified surface exhibits "self-cleaning" properties (dirt removal via water rinsing, e.g. from rainwater) and/or soil release benefits (top layers are strippable via mild mechanical action).

**[00122]** In contrast to hydrophilic modification with organic polymers, the benefits provided by nanoparticles, such as LAPONITE®, either alone or in combination with a charged modifier, are longer lived. For example, sheeting/anti-spotting benefits are maintained on an automobile body and glass window after multiple rinses versus the duration of such benefits after only about one rinse with tap water or rainwater on a surface coated with hydrophilic polymer technology.

#### Substances Generally Recognized As Safe

**[00123]** Compositions according to the invention may comprise substances generally recognized as safe (GRAS), including essential oils, oleoresins (solvent-free) and natural extractives (including distillates), and synthetic flavoring materials and adjuvants. Compositions may also comprise GRAS materials commonly found in cotton, cotton textiles, paper and paperboard stock dry food packaging materials (referred herein as substrates) that have been found to migrate to dry food and, by inference may migrate into the inventive compositions when these packaging materials are used as substrates for the inventive compositions.

**[00124]** Suitable GRAS materials are listed in the Code of Federal Regulations (CFR) Title 21 of the United States Food and Drug Administration, Department of Health and Human Services, Parts 180.20, 180.40 and 180.50, which are hereby incorporated by reference. These suitable GRAS materials include essential oils, oleoresins (solvent-free), and natural extractives (including distillates). The GRAS materials may be present in the compositions in amounts of up to about 10% by weight, preferably in amounts of 0.01 and 5% by weight.

**[00125]** Preferred GRAS materials include oils and oleoresins (solvent-free) and natural extractives (including distillates) derived from alfalfa, allspice, almond bitter (free from prussic acid), ambergris, ambrette seed, angelica, angostura (cusparia bark), anise, apricot kernel (persic oil), asafetida, balm (lemon balm), balsam (of Peru), basil, bay leave, bay (myrcia oil), bergamot (bergamot orange), bois de rose (Aniba rosaeodora Ducke), cacao, camomile (chamomile) flowers, cananga, capsicum, caraway, cardamom seed (cardamon), carob bean, carrot, cascarilla bark, cassia bark, Castoreum, celery seed, cheery (wild bark), chervil, cinnamon bark, Civet (zibeth, zibet, zibetum), ceylon (Cinnamomum zeylanicum Nees), cinnamon (bark and leaf), citronella, citrus peels, clary

(clary sage), clover, coca (decocainized), coffee, cognac oil (white and green), cola nut (kola nut), coriander, cumin (cummin), curacao orange peel, cusparia bark, dandelion, dog grass (quackgrass, triticum), elder flowers, estragole (esdragol, esdragon, estragon, tarragon), fennel (sweet), fenugreek, galanga (galangal), geranium, ginger, grapefruit, guava, hickory bark, horehound (hoarhound), hops, horsemint, hyssop, immortelle (*Helichrysum augustifolium* DC), jasmine, juniper (berries), laurel berry and leaf, lavender, lemon, lemon grass, lemon peel, lime, linden flowers, locust bean, lupulin, mace, mandarin (*Citrus reticulata* Blanco), marjoram, mate, menthol (including menthyl acetate), molasses (extract), musk (Tonquin musk), mustard, naringin, neroli (bigarade), nutmeg, onion, orange (bitter, flowers, leaf, flowers, peel), origanum, palmarosa, paprika, parsley, peach kernel (persic oil), pepper (black, white), peanut (stearine), peppermint, Peruvian balsam, petitgrain lemon, petitgrain mandarin (or tangerine), pimenta, pimenta leaf, pipsissewa leaves, pomegranate, prickly ash bark, quince seed, rose (absolute, attar, buds, flowers, fruit, hip, leaf), rose geranium, rosemary, saffron, sage, St. John's bread, savory, schinus molle (*Schinus molle* L), sloe berries, spearmint, spike lavender, tamarind, tangerine, tarragon, tea (*Thea sinensis* L.), thyme, tuberose, turmeric, vanilla, violet (flowers, leaves), wild cherry bark, ylang-ylang and zedoary bark.

**[00126]** Suitable synthetic flavoring substances and adjuvants are listed in the Code of Federal Regulations (CFR) Title 21 of the United States Food and Drug Administration, Department of Health and Human Services, Part 180.60, which is hereby incorporated by reference. These GRAS materials may be present in the compositions in amounts of up to about 1% by weight, preferably in amounts of 0.01 and 0.5% by weight.

**[00127]** Suitable synthetic flavoring substances and adjuvants that are generally recognized as safe for their intended use, include acetaldehyde (ethanal), acetoin (acetyl methylcarbinol), anethole (parapropenyl anisole), benzaldehyde (benzoic aldehyde), n-Butyric acid (butanoic acid), d- or l-carvone (carvol), cinnamaldehyde (cinnamic aldehyde), citral (2,6-dimethyloctadien-2,6-al-8, gera-nial, neral), decanal (N-decylaldehyde, capraldehyde, capric aldehyde, caprinaldehyde, aldehyde C-10), ethyl acetate, ethyl butyrate, 3-Methyl-3-phenyl glycidic acid ethyl ester (ethyl-methyl-phenyl-glycidate, so-called strawberry aldehyde, C-16 aldehyde), ethyl vanillin, geraniol (3,7-dimethyl-2,6 and 3,6-octadien-1-ol), geranyl acetate (geraniol acetate), limonene (d-, l-, and dl-), linalool (linalol, 3,7-dimethyl-1,6-octadien-3-ol), linalyl acetate (bergamol),

methyl anthranilate (methyl-2-aminobenzoate), piperonal (3,4-methylenedioxy-benzaldehyde, heliotropin) and vanillin.

**[00128]** Suitable GRAS substances that may be present in the inventive compositions that have been identified as possibly migrating to food from cotton, cotton textiles, paper and paperboard materials used in dry food packaging materials are listed in the Code of Federal Regulations (CFR) Title 21 of the United States Food and Drug Administration, Department of Health and Human Services, Parts 180.70 and 180.90, which are hereby incorporated by reference. The GRAS materials may be present in the compositions either by addition or incidentally owing to migration from the substrates to the compositions employed in the invention, or present owing to both mechanisms. If present, the GRAS materials may be present in the compositions in amounts of up to about 1% by weight.

**[00129]** Suitable GRAS materials that are suitable for use in the invention, identified as originating from either cotton or cotton textile materials used as substrates in the invention, include beef tallow, carboxymethylcellulose, coconut oil (refined), cornstarch, gelatin, lard, lard oil, oleic acid, peanut oil, potato starch, sodium acetate, sodium chloride, sodium silicate, sodium tripolyphosphate, soybean oil (hydrogenated), talc, tallow (hydrogenated), tallow flakes, tapioca starch, tetrasodium pyrophosphate, wheat starch and zinc chloride.

**[00130]** Suitable GRAS materials that are suitable for use in the invention, identified as originating from either paper or paperboard stock materials used as substrates in the invention, include alum (double sulfate of aluminum and ammonium potassium, or sodium), aluminum hydroxide, aluminum oleate, aluminum palmitate, casein, cellulose acetate, cornstarch, diatomaceous earth filler, ethyl cellulose, ethyl vanillin, glycerin, oleic acid, potassium sorbate, silicon dioxides, sodium aluminate, sodium chloride, sodium hexametaphosphate, sodium hydrosulfite, sodium phosphoaluminate, sodium silicate, sodium sorbate, sodium tripolyphosphate, sorbitol, soy protein (isolated), starch (acid modified, pregelatinized and unmodified), talc, vanillin, zinc hydrosulfite and zinc sulfate.

## Fragrance

[00131] Compositions of the present invention may comprise from about 0.01% to about 50% by weight of the fragrance oil. Compositions of the present invention may comprise from about 0.2% to about 25% by weight of the fragrance oil. Compositions of the present invention may comprise from about 1% to about 25% by weight of the fragrance oil.

[00132] As used herein the term "fragrance oil" relates to the mixture of perfume raw materials that are used to impart an overall pleasant odor profile to a composition. As used herein the term "perfume raw material" relates to any chemical compound which is odiferous when in an un-entrapped state, for example in the case of pro-perfumes, the perfume component is considered, for the purposes of this invention, to be a perfume raw material, and the pro-chemistry anchor is considered to be the entrapment material. In addition "perfume raw materials" are defined by materials with a ClogP value preferably greater than about 0.1, more preferably greater than about 0.5, even more preferably greater than about 1.0. As used herein the term "ClogP" means the logarithm to base 10 of the octanol/water partition coefficient. This can be readily calculated from a program called "CLOGP" which is available from Daylight Chemical Information Systems Inc., Irvine Calif., U.S.A. Octanol/water partition coefficients are described in more detail in U.S. Pat. No. 5,578,563.

[00133] The individual perfume raw materials which comprise a known natural oil can be found by reference to Journals commonly used by those skilled in the art such as "Perfume and Flavourist" or "Journal of Essential Oil Research". In addition some perfume raw materials are supplied by the fragrance houses as mixtures in the form of proprietary speciality accords. In order that fragrance oils can be developed with the appropriate character for the present invention the perfume raw materials have been classified based upon two key physical characteristics:

[00134] (i) boiling point (BP) measured at 1 atmosphere pressure. The boiling point of many fragrance materials are given in Perfume and Flavor Chemicals (Aroma Chemicals), Steffen Arctander (1969). Perfume raw materials for use in the present invention are divided into volatile raw materials (which have a boiling point of less than, or equal to, about 250° C.) and residual raw materials (which have a boiling point of

greater than about 250° C., preferably greater than about 275° C.). All perfume raw materials will preferably have boiling points (BP) of about 500° C. or lower.

**[00135]** (ii) odour detection threshold which is defined as the lowest vapour concentration of that material which can be olfactorily detected. The odour detection threshold and some odour detection threshold values are discussed in e.g., "Standardized Human Olfactory Thresholds", M. Devos et al, IRL Press at Oxford University Press, 1990, and "Compilation of Odor and Taste Threshold Values Data", F. A. Fazzalar, editor ASTM Data Series DS 48A, American Society for Testing and Materials, 1978, both of said publications being incorporated by reference. Perfume raw materials for use in the present invention can be classified as those with a low odour detection threshold of less than 50 parts per billion, preferably less than 10 parts per billion and those with a high odour detection threshold which are detectable at greater than 50 parts per billion (values as determined from the reference above).

**[00136]** Since, in general, perfume raw materials refer to a single individual compound, their physical properties (such ClogP, boiling point, odour detection threshold) can be found by referencing the texts cited above. In the case that the perfume raw material is a natural oil, which comprises a mixture of several compounds, the physical properties of the complete oil should be taken as the weighted average of the individual components. In the case that the perfume raw material is a proprietary speciality accord the physical properties should be obtain from the Supplier.

**[00137]** In general a broad range of suitable perfume raw materials can be found in U.S. Pat. Nos. 4,145,184, 4,209,417, 4,515,705, and 4,152,272. Non- limiting examples of perfume raw materials which are useful for blending to formulate fragrance oils for the present invention are given below. Any perfume raw materials, natural oils or proprietary speciality accords known to a person skilled in the art can be used within the present invention.

**[00138]** Volatile perfume raw materials useful in the present invention are selected from, but are not limited to, aldehydes with a relative molecular mass of less than or equal to about 200, esters with a relative molecular mass of less than or equal to about 225, terpenes with a relative molecular mass of less than or equal to about 200, alcohols with a relative molecular mass of less than or equal to about 200 ketones with a relative



molecular mass of less than or equal to about 200, nitriles, pyrazines, and mixtures thereof.

**[00139]** Examples of volatile perfume raw materials having a boiling point of less than, or equal to, 250° C., with a low odor detection are selected from, but are not limited to, anethol, methyl heptine carbonate, ethyl aceto acetate, para cymene, nerol, decyl aldehyde, para cresol, methyl phenyl carbiny acetate, ionone alpha, ionone beta, undecylenic aldehyde, undecyl aldehyde, 2,6-nonadienal, nonyl aldehyde, octyl aldehyde. Further examples of volatile perfume raw materials having a boiling point of less than, or equal to, 250° C., which are generally known to have a low odour detection threshold include, but are not limited to, phenyl acetaldehyde, anisic aldehyde, benzyl acetone, ethyl-2- methyl butyrate, damascenone, damascone alpha, damascone beta, flor acetate, frutene, fructose, herbavert, iso cyclo citral, methyl isobutenyl tetrahydro pyran, iso propyl quinoline, 2,6- nonadien-1-ol, 2- methoxy-3-(2-methylpropyl)-pyrazine, methyl octine carbonate, tridecene-2- nitrile, allyl amyl glycolate, cyclogalbanate, cyclal C, melonal, gamma nonalactone, cis 1,3-oxathiane-2-methyl-4-propyl.

**[00140]** Other volatile perfume raw materials having a boiling point of less than, or equal to, 250° C., which are useful in the present invention, which have a high odor detection threshold, are selected from, but are not limited to, benzaldehyde, benzyl acetate, camphor, carvone, borneol, bornyl acetate, decyl alcohol, eucalyptol, linalool, hexyl acetate, iso-amyl acetate, thymol, carvacrol, limonene, menthol, iso-amyl alcohol, phenyl ethyl alcohol, alpha pinene, alpha terpineol, citronellol, alpha thujone, benzyl alcohol, beta gamma hexenol, dimethyl benzyl carbinol, phenyl ethyl dimethyl carbinol, adoxal, allyl cyclohexane propionate, beta pinene, citral, citronellyl acetate, citronellal nitrile, dihydro myrcenol, geraniol, geranyl acetate, geranyl nitrile, hydroquinone dimethyl ether, hydroxycitronellal, linalyl acetate, phenyl acetaldehyde dimethyl acetal, phenyl propyl alcohol, prenyl acetate, triplal, tetrahydrolinalool, verdox, cis-3-hexenyl acetate.

**[00141]** Examples of residual "middle and base note" perfume raw materials having a boiling point of greater than 250° C., which have a low odor detection threshold are selected from, but are not limited to, ethyl methyl phenyl glycidate, ethyl vanillin, heliotropin, indol, methyl anthranilate, vanillin, amyl salicylate, coumarin. Further examples of residual perfume raw materials having a boiling point of greater than 250° C.

which are generally known to have a low odour detection threshold include, but are not limited to, ambrox, bacdanol, benzyl salicylate, butyl anthranilate, cetalex, ebanol, cis-3-hexenyl salicylate, lilial, gamma undecalactone, gamma dodecalactone, gamma decalactone, calone, cymal, dihydro iso jasmonate, iso eugenol, lyral, methyl beta naphthyl ketone, beta naphthol methyl ether, para hydroxyl phenyl butanone, 8-cyclohexadecen-1-one, oxocyclohexadecen-2-one/habanolide, florhydral, intrelvein aldehyde.

[00142] Other residual "middle and base note" perfume raw materials having a boiling point of greater than 250° C. which are useful in the present invention, but which have a high odour detection threshold, are selected from, but are not limited to, eugenol, amyl cinnamic aldehyde, hexyl cinnamic aldehyde, hexyl salicylate, methyl dihydro jasmonate, sandalore, veloutone, undecavertol, exaltolide/cyclopentadecanolide, zingerone, methyl cedrylone, sandela, dimethyl benzyl carbinyl butyrate, dimethyl benzyl carbinyl isobutyrate, triethyl citrate, cashmeran, phenoxy ethyl isobutyrate, iso eugenol acetate, helional, iso E super, ionone gamma methyl, pentalide, galaxolide, phenoxy ethyl propionate.

#### Entrapment Material

[00143] Compositions of the present invention may comprise an entrapment material at a level of from about 0.1% to about 95%, or from about 0.5% to about 50%, or from about 1% to about 25% by weight, of an entrapment material.

[00144] As defined herein an "entrapment material" is any material which, after application of the composition to a substrate, suppresses the volatility of the perfume raw materials within the fragrance oil thus delaying their evaporation. It is not necessary that the entrapment material forms an association with the perfume raw material within the composition itself, only that this association exists on the substrate after application of the composition. Non-limiting examples of mechanisms by which the delay in evaporation may occur are by the entrapment material reversibly or irreversibly, physically or chemically associating with the perfume raw material through complexing, encapsulating, occluding, absorbing, binding, or otherwise adsorbing the perfume raw materials of the fragrance oil.

[00145] As defined herein "reversible entrapment" means that any entrapment material: perfume raw material association in which the association can be broken down so that the entrapment material and perfume raw materials are released from each other. As defined herein "irreversible entrapment" means that the entrapment material: perfume raw material association cannot be broken down. As defined herein "chemically associated" means that the entrapment material and perfume raw material are linked through a covalent, ionic, hydrogen or other type of chemical bond. As defined herein "physically associated" means that the entrapment material and perfume raw material are linked through a bond with a weaker force such as a Van der Waals force. Highly preferred is that, upon the substrate, the entrapment material and the perfume raw material form a reversible physical or chemical association.

[00146] As defined herein "to delay the evaporation of a perfume raw material" means to slow down or inhibit the evaporation rate of said perfume raw material from the substrate such that the fragrance "top note" character of the perfume raw material is detectable for at least 2 hours after application to the substrate.

[00147] Entrapment materials for use herein are selected from polymers; capsules, microcapsules and nanocapsules; liposomes; pro-perfumes selected from more than 1 type of pro-chemistry; film formers; absorbents; cyclic oligosaccharides and mixtures thereof. Suitable examples are pro-perfumes selected from more than 1 type of pro-chemistry, absorbents and cyclic oligosaccharides and mixtures thereof.

[00148] Within the entrapment association, the weight ratio of top note perfume raw material to entrapment material within the associated form may be in the range from about 1:20 to about 20:1, or in the range from about 1:10 to about 10:1, or in the range from about 1:10 to about 1:4.

[00149] It is suitable for compositions of the present invention that the entrapment material reversibly, chemically and physically complexes the perfume raw materials. Non-limiting examples of entrapment materials that can act in this way are cyclic oligosaccharides, or mixtures of different cyclic oligosaccharides.

[00150] As used herein, the term "cyclic oligosaccharide" means a cyclic structure comprising six or more saccharide units. Suitable for use herein are cyclic

oligosaccharides having six, seven or eight saccharide units and mixtures thereof, or six or seven saccharide units, or seven saccharide units. It is common in the art to abbreviate six, seven and eight membered cyclic oligosaccharides to  $\alpha$ ,  $\beta$  and  $\gamma$  respectively.

**[00151]** The cyclic oligosaccharide of the compositions used for the present invention may comprise any suitable saccharide or mixtures of saccharides. Examples of suitable saccharides include, but are not limited to, glucose, fructose, mannose, galactose, maltose and mixtures thereof. Suitable for use herein are cyclic oligosaccharides of glucose. Suitable cyclic oligosaccharides for use herein are  $\alpha$ -cyclodextrins or  $\beta$ -cyclodextrins, or mixtures thereof, and also suitable cyclic oligosaccharides for use herein are  $\beta$ -cyclodextrins.

**[00152]** The cyclic oligosaccharide, or mixture of cyclic oligosaccharides, for use herein may be substituted by any suitable substituent or mixture of substituents. Herein the use of the term "mixture of substituents" means that two or more different suitable substituents can be substituted onto one cyclic oligosaccharide. The derivatives of cyclodextrins consist mainly of molecules wherein some of the OH groups have been substituted. Suitable substituents include, but are not limited to, alkyl groups; hydroxyalkyl groups; dihydroxyalkyl groups; (hydroxyalkyl)alkylenyl bridging groups such as cyclodextrin glycerol ethers; aryl groups; maltosyl groups; allyl groups; benzyl groups; alkanoyl groups; cationic cyclodextrins such as those containing 2-hydroxy-3-(dimethylamino) propyl ether; quaternary ammonium groups; anionic cyclodextrins such as carboxyalkyl groups, sulphobutylether groups, sulphate groups, and succinylates; amphoteric cyclodextrins; and mixtures thereof. Other cyclodextrin derivatives are disclosed in copending U.S. application Ser. No. 09/32192 (May 27, 1999), all of which are incorporated herein by reference.

**[00153]** The substituents may be saturated or unsaturated, straight or branched chain. Suitable substituents include saturated and straight chain alkyl groups, hydroxyalkyl groups and mixtures thereof. Suitable alkyl and hydroxyalkyl substituents are selected from C 1-C8 alkyl or hydroxyalkyl groups or mixtures thereof, or suitable alkyl and hydroxyalkyl substituents are selected from C 1-C6 alkyl or hydroxyalkyl groups or mixtures thereof, or suitable alkyl and hydroxyalkyl substituents are selected from C 1-C4 alkyl or hydroxyalkyl groups and mixtures thereof. Suitable alkyl and

hydroxyalkyl substituents are propyl, ethyl and methyl, or hydroxypropyl and methyl, or methyl.

**[00154]** Suitable cyclic oligosaccharides for use in the present invention are unsubstituted, or are substituted by only saturated straight chain alkyl, or hydroxyalkyl substituents. Therefore, suitable examples of cyclic oligosaccharides for use herein are  $\alpha$ -cyclodextrin,  $\beta$ -cyclodextrin, methyl- $\alpha$ -cyclodextrin, methyl- $\beta$ -cyclodextrin, hydroxypropyl- $\alpha$ -cyclodextrin and hydroxypropyl- $\beta$ -cyclodextrin. Suitable examples of cyclic oligosaccharides for use herein are methyl- $\alpha$ -cyclodextrin and methyl- $\beta$ -cyclodextrin. These are available from Wacker-Chemie GmbH Hanns-Seidel-Platz 4, Munchen, DE under the tradename Alpha W6 M and Beta W7 M respectively. Suitable is methyl- $\beta$ -cyclodextrin.

**[00155]** Methods of modifying cyclic oligosaccharides are well known in the art. For example, see "*Methods of Selective Modifications of Cyclodextrins*" *Chemical Reviews* (1998) Vol. 98, No. 5, pp 1977-1996, Khan et al and U.S. Pat. No. 5, 710,268.

**[00156]** In addition to suitable substituents themselves, it is also suitable that the cyclic oligosaccharides of the compositions used for the present invention have an average degree of substitution of at least 1.6, wherein the term "degree of substitution" means the average number of substituents per saccharide unit. Suitable cyclic oligosaccharides for use herein have an average degree of substitution of less than about 2.8. Suitable cyclic oligosaccharides for use herein have an average degree of substitution of from about 1.7 to about 2.0. The average number of substituents can be determined using common Nuclear Magnetic Resonance techniques known in the art.

**[00157]** The cyclic oligosaccharides of the compositions used for the present invention may be soluble in both water and ethanol. As used herein "soluble" means at least about 0.1 g of solute dissolves in 100 ml of solvent, at 25° C. and 1 atm of pressure. Suitable cyclic oligosaccharides for use herein have a solubility of at least about 1 g/100ml, at 25° C. and 1 atm of pressure. Suitable cyclic oligosaccharides may only be present at levels up to their solubility limits in a given composition at room temperature. A person skilled in the art will recognise that the levels of cyclic oligosaccharides used in the present invention will also be dependent on the components of the composition and their levels, for example the solvents used or the exact fragrance oils, or combination of

fragrance oils, present in the composition. Therefore, although the limits stated for the entrapment material are suitable, they are not exhaustive.

**[00158]** Encapsulation of fragrances within capsules, micro- capsules or nanaocapsules, which are broken down by environmental triggers, can be used to reduce the volatility of fragrance oils by surrounding the oil by small droplets as a resistant wall. This may be either water sensitive or insensitive. In the first case the fragrance is released when the encapsulated particle is affected by moisture loss from the skin; while in the second case the capsule wall must be ruptured mechanically before the fragrance is released. Encapsulation techniques are well known in the art including DE 1,268,316; U.S. Pat. Nos. 3,539,465; 3,455,838.

**[00159]** Moisture sensitive capsules, micro-capsules and nanocapsules are preferably formed from, but not limited to, a polysaccharide polymer. Examples of suitable polymers are dextrans, especially low-viscosity dextrans including maltodextrans. A particularly preferred example of a low viscosity dextrin is one which, as a 50% dispersion in water has a viscosity at 25° C., using a Brookfield Viscometer fitted with an "A" type T-Bar rotating at 20 rpm in helical mode, of 330±20 mPa.s. This dextrin is known as Encapsul 855 and is available from National Starch and Chemicals Ltd. A further example of a polysaccharide that can be used to form the moisture sensitive capsules is gum acacia.

**[00160]** Time release micro-capsules are also suitable for use in compositions of the present invention for entrapping hydrophobic perfume raw materials. Such compositions comprise the perfume raw materials encapsulated in a wax or polymer matrix which in turn is coated with a compatible surfactant. The wax or polymers used to form the matrix have a melting point in the range from about 35° C. to about 120° C. at 1 atmosphere pressure. These are described in detail in EP-A-908,174.

**[00161]** Film formers can also be used to reduce the volatility profile of perfume raw materials. When the fragrance is applied to a substrate, such as the skin, it is believed that film formers entrap the perfume oils during the evaporation of the volatile solvent thus hindering the release of the volatile material. Any film former, which is compatible with the perfume raw materials, may be used, preferably the film former will be soluble in water-ethanol mixture. Film former materials useful in this invention include, but are not

limited to, ionic and non-ionic derivatives of water-soluble polymers. Examples of suitable film forming materials are water-soluble polymers containing a cationic moiety such as polyvinyl pyrrolidine and its derivatives having a molecular weight of 50,000 to 1,000,000. Other examples of ionic polymeric film forming materials are cationic cellulose derivatives sold under the trade names of Polymer JR (union Carbide), Klucel GM (hercules) and ethoxylated polyethyleneimine sold under the trade name PEI 600 (Dow). Examples of suitable cellulosic derivatives such as hydroxymethyl cellulose, hydroxypropyl methylcellulose and hydroxyethyl cellulose. Another examples of film formers is benzophenone. Non-limiting examples of film forming materials are given in U.S. Pat. No. 3,939,099.

**[00162]** Additional non-limiting examples of other polymer systems that can be used include water soluble anionic polymers e.g., polyacrylic acids and their water-soluble salts are useful in the present invention to delay the evaporation rate of certain amine-type odours. Suitable polyacrylic acids and their alkali metal salts have an average molecular weight of less than about 20,000, or less than 10,000, or from about 500 to about 5,000. Polymers containing sulphonic acid groups, phosphoric acid groups, phosphonic acid groups and their water-soluble salts, and their mixtures thereof, and mixtures with carboxylic acid and carboxylate groups, are also suitable.

**[00163]** Water-soluble polymers containing both cationic and anionic functionalities are also suitable. Examples of these polymers are given in U.S. Pat. No. 4,909,986. Another example of water-soluble polymers containing both cationic and anionic functionalities is a copolymer of dimethyldiallyl ammonium chloride and acrylic acid, commercially available under the trade name Merquat 280® from Calgon.

**[00164]** Synthesising pro-perfumes or pro-fragrances from perfume raw materials can result in compounds which impart a delayed release mechanism to that specific perfume raw material. Pro-perfumes useful within the present invention include those selected from more than 1 type of pro-chemistry which ensures that a wide range of possible perfume raw materials can be used. This is consistent with the objective of providing unique fragrances with a broad spectrum of "top note" characters.

**[00165]** Within a pro-perfume the perfume raw material has been reacted with more than one type of chemical groups such as acetal, ketal, ester, hydrolysable inorganic-

organic. As such, as defined within the present invention, the perfume raw material is considered to constitute part of the fragrance oil and the chemical groups to constitute part of the entrapment material. Pro-perfumes themselves are designed to be non-volatile, or else have a very low volatility. However, once on the substrate, the perfume raw material is released from the pro-perfume. Once released the perfume raw material has its original characteristics. The perfume raw material may be released from the pro-perfume in a number of ways. For example, it may be released as a result of simple hydrolysis, or by shift in an equilibrium reaction or by a pH-change, or by enzymatic release. The fragrances herein can be relatively simple in their compositions, comprising a single chemical, or can comprise highly sophisticated complex mixtures of natural and synthetic chemical components, all chosen to provide any desired odor. Non-limiting pro-perfumes suitable for use in the present application are described in WO 98/47477, WO 99/43667, WO 98/07405, WO 98/47478.

**[00166]** When clarity of solution is not needed, odor-absorbing materials such as zeolites and/or activated carbon can be used to modify the release rate of perfume raw materials.

**[00167]** A suitable class of zeolites is characterised as "intermediate" silicate/aluminate zeolites. The intermediate zeolites are characterised by SiO<sub>2</sub>/AlO<sub>2</sub> molar ratios of less than about 10, preferably in the range from about 2 to about 10. The intermediate zeolites have an advantage over the "high" zeolites since they have an affinity for amine-type odors, they are more weight efficient for odor absorption since they have a larger surface area and they are more moisture tolerant and retain more of their odour absorbing capacity in water than the high zeolites. A wide variety of intermediate zeolites suitable for use herein are commercially available as Valfor® CP301-68, Valfor® 300-63, Valfor® CP300-35 and Valfor® 300-56 available from PQ Corporation, and the CBV100® series of zeolites from Conteka. Zeolite materials marketed under the trade name Abscents® and Smellrite® available from The Union Carbide Corporation and UOP are also suitable. These materials are typically available as a white powder in the 3-5 µm particle size range.

**[00168]** Carbon materials suitable for use in the present invention are materials well known in commercial practice as absorbents for organic molecules and/or for air



purification purposes. Often, such carbon material is referred to as "activated" carbon or "activated charcoal". Such carbon is available from commercial sources under trade names as; Calgon-Type CPG®; Type PCB®; Type SGL®; Type CAL®; and Type OL®.

[00169] Other odor absorbers suitable for use herein include silica molecular sieves, activated alumina, bentonite and kaolinite.

[00170] When cyclic oligosaccharides are present in the compositions of the present invention, low molecular weight polyol molecular wedge having from about 2 to about 12 carbon atoms, or from about 2 to about 6 carbon atoms and at least one --OH functional group, or at least 2 --OH functional groups are used herein for further prolonging the fragrance character of the composition. These polyols can further contain ether groups within the carbon chain. Suitable examples include ethylene glycol, propylene glycol, dipropylene glycol, 1,4- butanediol, 1,6-hexanediol and mixtures thereof. When present these polyols are present at a level of from about 0.01% to about 20%, or from about 0.1% to about 10%, or from about 0.5% to about 5% by weight of composition. It is suitable that the molar ratio of molecular wedge material to oligosaccharide is from 10:1 to 1:10, preferably 1:1 or greater, especially 1:1.

[00171] Compositions and fragrance oils for use in the present invention should be prepared according to procedures usually used in and that are well known and understood by those skilled in the art with materials of similar phase partitioning can be added in any order. The entrapment of the perfume raw materials can occur at any reasonable stage in the preparation of the overall composition. As such the fragrance oil can be prepared in its entirety, then entrapped with a suitable material before addition to the remainder of the composition. Alternatively the entrapment material can be added to the balance of the composition prior to addition of the complete fragrance oil. Finally it is possible to entrap any single perfume raw material, or group of raw materials, individually before either adding these to the balance of the fragrance oil or to the balance of the composition. Preparation of specific fragrance compositions is described in US2003/0211125.

#### Water

[00172] Since the composition is an aqueous composition, water can be, along with the solvent, a predominant ingredient. The water should be present at a level of less than

99.9%, more preferably less than about 99%, and most preferably, less than about 98%. Deionized water is preferred. Where the cleaning composition is concentrated, the water may be present in the composition at a concentration of about 5 wt. % to 70 wt. %.

#### Method of Use

**[00173]** The aerosol carpet cleaning composition can be used as a method of cleaning carpets by applying the aerosol carpet cleaning composition to the carpet, wiping the carpet with a cleaning implement comprising a disposable cleaning substrate, and allowing the carpet to dry.

**[00174]** More specifically, for SPOT & STAIN CLEANING:

1. Squeeze trigger and apply aerosol carpet cleaner directly onto stain. Avoid saturating carpet. Tough stains should be sprayed and allowed to stand several minutes to allow aerosol carpet cleaner to loosen the stain.
2. Scrub carpet surface by working foam into the carpet using the cleaning implement with a disposable cleaning pad with a criss-cross mopping motion. Repeat Steps 1 & 2 as needed.
3. Allow carpet to dry before walking or sitting on carpet. Drying time can vary due to humidity and depth of carpet pile.

**[00175]** For CLEANING LARGER AREA:

1. Squeeze trigger and apply aerosol carpet cleaner onto carpet while scrubbing carpet surface with a criss-cross mopping motion with the cleaning implement with a disposable cleaning pad.
2. Continue working across the carpet until the entire area is cleaned.
3. Allow carpet to dry before walking or sitting on carpet. Drying time can vary due to humidity and depth of carpet pile.

**[00176]** The aerosol carpet cleaning composition can be used as a method of cleaning carpets by applying the aerosol carpet cleaning composition to the carpet,

optionally wiping the carpet with a substrate, allowing the carpet to dry, and optionally vacuuming.

Article of Manufacture

**[00177]** The aerosol carpet cleaning composition may be part of an article of manufacture comprising: a cleaning implement; a disposable cleaning pad; an aerosol cleaning composition; and a set of instructions comprising the steps of: applying an aerosol carpet cleaning composition to the carpet, wiping the carpet with a cleaning implement comprising a disposable cleaning substrate, and allowing the carpet to dry.

**[00178]** The aerosol carpet cleaning composition may be part of an article of manufacture comprising an aerosol composition in a canister for use on carpets and not requiring a cleaning implement.

## EXAMPLES

**[00179]** Examples of suitable aerosol cleaning compositions are provided in Tables I, II, and III.

**[00180]** Table I

	Example A #1	Example B #3	Example C #5	Example D #6	Example E #9
Ethylene glycol monohexyl ether <sup>a</sup>		1.00%	1.00%	0.50%	
DPnP <sup>b</sup>	10.00 %	5.00%	5.00%	10.00%	5.00%
Sodium lauryl sulfate <sup>c</sup>	0.29%	0.58%	0.29%	0.58%	0.29%
Sodium borate decahydrate	0.60%	0.30%	0.30%	0.30%	0.30%
Stain resist <sup>d</sup>	0.05%	0.05%	0.05%	0.05%	0.05%
Fluorosurfactant <sup>e</sup>	0.04%	0.04%		0.04%	0.08%
Sodium nitrite	0.25%	0.25%	0.25%	0.25%	0.25%
Ammonium hydroxide	0.028%	0.028%	0.028%	0.028%	0.028%
Propellant	5.00%	5.00%	5.00%	5.00%	5.00%
Water	Balance	Balance	Balance	Balance	Balance
Foam density g/100 cc	3.99	4.68	12.19	5.53	3.85
Foam breaks in beaker	32 min	21 min	20 min	6 min	71 min

- a. from Union Carbide
- b. Dipropylene glycol n-propyl ether from Arco Chemical
- c. Stepanol WAC (29%) from Stepan Company
- d. Zelan 338 (25%) from DuPont
- e. Zonyl FSO (50%) from DuPont

[00181]

Table II

	Example F #13	Example G #14	Example H #15	Example I #23	Comparative Commercial Example #1
Ethylene glycol monohexyl ether	1.00%		0.50%		
DPnP	10.00 %			5.00%	
Sodium lauryl sulfate	0.29%	0.29%		0.29%	
Sodium borate decahydrate	0.30%	0.30%	0.30%	0.30%	
Stain resist	0.05%	0.05%	0.05%	0.05%	
Fluorosurfactant	0.04%	0.04%	0.04%		
Sodium nitrite	0.25%	0.25%	0.25%	0.25%	
Ammonium hydroxide	0.028%	0.028%	0.028%	0.028%	
Propellant	5.00%	5.00%	5.00%	5.00%	
Water	Balance	Balance	Balance	Balance	
Foam density g/100 cc	8.07	8.14	6.52	4.68	2.25
Foam breaks in beaker	4 min	220 min	240 min	32 min	86 min

**[00182]**      Table III

	Example J TC-1	Example K	Example L		
Ethylene glycol monohexyl ether		5.00%	5.00%		
Propylene glycol phenyl ether	8.00 %	5.00%	5.00%		
Sodium lauryl sulfate	0.29%				
Sodium borate decahydrate	0.60%	0.60%	0.60%		
Stain resist	0.05%	1.00%	10.00%		
Fluorosurfactant					
Sodium nitrite	0.25%	0.25%	0.25%		
Ammonium hydroxide	0.028%	0.028%	0.028%		
Fragrance	0.10%	0.10%	0.10%		
Propellant	5.00%	5.00%	5.00%		
Water	Balance	Balance	Balance		
Foam density					

**[00183]**      Foam Break Time. A fixed volume (40 ml) of foam was sprayed on a carpet for the Inventive Example J and a Comparative Commercial Example #1. The foam was spray on two different nylon, cut pile, 0.5 inch carpets (Mohawk: Endurance Plus – Face Weight: 42.0 and Shaw: TM 155 – Face Weight: 25.0). Based on the foam densities, 40 ml of product is equivalent to 2.02g (density = 5.06 g/cc) of the Inventive Example J and 1.18g of the Comparative Commercial Example #1 (density = 2.96 g/cc). A different Comparative Commercial Example #2 was also sprayed under the same conditions. The time was recorded for the foam to break completely (no more foam could be seen on top the carpet) and is shown in Table IV.

**[00184]**

[00185] Table IV

	Mohawk Carpet	Shaw Carpet
Inventive Example J	78 sec	120 sec
Comparative Example #1	837 sec	856 sec
Comparative Example #2	1 sec	1 sec

[00186] Foam Penetration. Acid Red dye 131 was added to the Inventive Example J in order to see the foam penetration into the carpet fibers. Approximately 25 grams of product was sprayed onto a 16"x16" carpet (0.1g/sq in). Two scenarios were tested where after spraying, the foam was left to dry or it was scrubbed (forward and backward 10 times, then right and left 10 times) with a cleaning tool as described in Copending Application U.S. Serial No.10/345,655 filed on January 16, 2003. After the samples were dry, 10 random fiber samples were cut from the pile and the distance of the dye penetration was measured.

[00187] Table V

	Mohawk Carpet	Shaw Carpet
Inventive Example J (spray only)	0.26 inches	0.23 inches
Inventive Example J (spray and scrub)	0.28 inches	0.31 inches
Comparative Example (spray only)		
Comparative Example (spray and scrub)		

[00188] Resoiling. The formulas were tested for resoiling after application of the carpet treatments, followed by a fixed amount of actual foot traffic. The carpet used for this study is Mohawk Endurance Plus with the color of Merange. The carpet samples were vacuumed and then 24 grams of product was applied onto a 10"x24" carpet. After each of the Inventive Examples and the water treatment were sprayed onto the carpet, the carpet was scrubbed with the cleaning implement with 20 strokes. The Commercial Aerosol was applied following the directions, which did not involve using a cleaning implement.

**[00189]** The carpets were measured for change of color using an Applied Color Systems Chroma Sensor CS3 spectrophotometer (Hunter difference, 10.degree. observer) using a Cool White Fluorescent light source. The change in color was measured using the L.a.b. color scale and calculated as delta E in Table VI. The L.a.b. scale is an industry standard used for the measurement of color. It is comprised of 3 perpendicular color axes (L, a and b), which define a three-dimensional color space. Delta E averages the reflectance changes of an item prior to and after use according to:

$$\text{Delta E} = [(L_u - L_n)^2 + (a_u - a_n)^2 + (b_u - b_n)^2]^{1/2}, \text{ where: } L = \text{reflectance};$$

a=redness/greenness; b=yellowness/blueness; u=carpet after treatment and traffic;  
n=carpet before treatment and traffic.

**[00190]** Table VI

	Delta E
Commercial Aerosol	6.48
Water	4.22
No Treatment	3.29
Example J	2.23
Example J with 1% Zelan 338	2.50

**[00191]** Disposable cleaning substrate K in Table VII was prepared with a distinct top layer and a distinct bottom layer using airlaid techniques with cellulosic fiber (pulp), bicomponent fiber (Bico) and high denier thermoplastic polyester fiber (PET). A latex binder ( $T_g = +5^{\circ}\text{C}$ ) was applied to bind the substrate together.

**[00192]** Mop pads were formed by combining the disposable cleaning substrate cover layer (Example K) with a pulp/bicomponent (Bico) fiber absorbent layer (250 gsm comprising 84% pulp fiber, 9% bicomponent fiber, and 7% of a polypropylene carrier layer) and a polyethylene (PE) film backsheet.

**[00193]** The disposable cleaning substrate L in Table VII was formed as unitized substrates combining the cover layer with the absorbent layer in one step.

**[00194]**



**[00195]**      Table VII

	Top layer nonwoven	Bottom layer nonwoven	Total substrate	Total Absorbency g/g
Example K 1.0 mm caliper	15 gsm PET 2 gsm Bico	40 gsm pulp 5 gsm Bico	8 gsm latex 40 gsm pulp 15 gsm PET 7 gsm Bico	7.58
Example L 2.5 mm caliper	15 gsm PET 5 gsm Bico	2 layers of 92 gsm pulp 10 gsm Bico	8 gsm latex 184 gsm pulp 15 gsm PET 25 gsm Bico	15.40

**[00196]**      Without departing from the spirit and scope of this invention, one of ordinary skill can make various changes and modifications to the invention to adapt it to various usages and conditions. As such, these changes and modifications are properly, equitably, and intended to be, within the full range of equivalence of the following claims.